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BATCH LEACHING OF GOLD IN CUPRIC CHLORIDE MEDIA

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Abstract

Gold is a noble metal, which has been traditionally leached with cyanidation. Nowadays this process is started objected for reconsideration due to toxicity, while alternative methods are pursued. Gold can be leached in acidic environment in the presence of oxidant and halides as complexing agent. Cupric chloride media is a suitable option for gold leaching as it offers rapid dissolution rate and less environmental risks related to leaching chemicals. Additionally, several of current gold reserves are challenging to leach with cyanide, whereas chloride leaching can offer a possible alternative method e.g. for high copper or refractory gold ore leaching. The major deficiency for chloride leaching is the instability of gold chloride complexes.

In this thesis, the parameters affecting gold dissolution in cupric chloride media are investigated with batch leaching experiments to determine optimal conditions, and to pursue an alternative for cyanidation. These parameters include leaching duration, circumferential speed, particle size, cupric concentration, chloride concentration and temperature, with two different low-grade raw materials, which are labeled raw material 1 and raw material 2. Additionally, silver extraction was investigated in the leaching process.

The laboratory results indicate that chloride concentration is the most consequential parameter and increasing it, increases gold extraction near linearly. Fine particle size and circumferential speed were both noted to have strictly positive effect on gold dissolution rates. The effect of cupric concentration depended on the raw material, as too high concentration reduced gold extraction rate. Therefore, the optimal concentration for raw material 1 is near 1 M and for raw material 2 between 0.5 M and 0.75 M. On contrary to literature, change in temperature from 65 to 95 °C was noted to have an unclear effect. Silver dissolution was more rapid than gold dissolution, yet there was little consistency.

Keywords Gold extraction, halide, cyanide-free, dissolution rate

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Tiivistelmä

Kulta on jalometalli, jota on perinteisesti liuotettu syanidin avulla. Nykyään prosessia halutaan rajoittaa myrkyllisyyden takia, joten vaihtoehtoisia keinoja tutkitaan jatkuvasti. Kultaa voidaan liuottaa happamassa ympäristössä hapettimen ja kompleksoivien aineiden, kuten halidien, kanssa. Kuparikloridiliuos soveltuu hyvin kullanliuotukseen liukenemisnopeuden ja vähäisempien ympäristöhaittojen takia. Lisäksi nykyisiä kultavarantoja on haastava liuottaa nykyisillä syanidimetodeilla, jolloin kloridiliuotus tarjoaa varteenotettavan vaihtoehdon. Merkittävin heikkous kloridiliuotuksessa on kuitenkin kultakloridikompleksien epävakaisuus.

Tässä diplomityössä tutkitaan kullan kuparikloridiliuotukseen liittyviä parametreja panosliuotuskokeiden avulla, selvittääkseen optimiolosuhteet kullan liukenemiseen ja löytämään vaihtoehtoja syanidille. Näihin parametreihin lukeutuvat liuotusaika, sekoitusnopeus, partikkelikoko, kupri-ionikonsentraatio, kloridi-ionikonsentraatio ja lämpötila kahdella eri raaka-aineella; raaka-aine 1 ja raaka-aine 2. Hopean liukenemista tutkittiin samalla.

Laboratoriotestien tulokset osoittavat, että kloridi-ionikonsentraatio on merkittävin tekijä eli sen kasvattaminen lisää kullan liukenemista lähes lineaarisesti. Pienellä partikkelikoolla ja suurella sekoitusnopeudella oli myös selkeästi positiivinen vaikutus kullan liukenemisnopeuteen. Kupari-ionikonsentraation vaikutus riippui raaka-aineesta, ja kupari-ionien liiallinen määrä vähensi kullan liukenemista. Optimaalinen konsentraatio on kuitenkin 1 M raaka-aineelle 1 sekä 0.5 ja 0.75 M välillä raaka-aineelle 2. Vastoin kirjallisuutta, lämpötilan muutos 65 °C:sta 95 °C:een oli kyseenalaista. Hopean liukeneminen oli lähtökohtaisesti nopeampaa kuin kullan liukeneminen, tosin tulokset olivat epäjohdonmukaisempia.

Avainsanat Kullan liuotus, halidit, syanidivapaa, liukenemisnopeus

FOREWORD

This Master's thesis was carried out in department of chemical and metallurgical Engineering at Aalto University's School of chemical technology between June 2017 and May 2018. This thesis was part of Outotec Inc's AuChloride research project and I would like to thank Outotec and Tekes for financing this thesis.

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I want to thank the whole research group. Furthermore, special thanks go to my colleagues in the same room; Tuomas, Sami, Elina and Jon. Thanks all for making it such a great experience.

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Espoo, 30th of March, 2018

Tero Junnila

Contents

I THEORETICAL PART

1 Introduction

Gold is known for occurring as a native metal in nature. This is primarily due to it being a noble metal. Furthermore, gold is durable and highly resistant to corrosion. However, the dissolution of gold is possible with appropriate complexing agents and oxidants. (Nicol, 1980; Marsden & House, 2006) Gold dissolves only in oxidizing solutions, which contain complexing ligands such as cyanide, halides, thiosulfate, thiourea and thiocyanate. This has also been beneficial as it allows gold to be extracted very selectively from ores. (Marsen & House, 2006)

Cyanidation is currently the most prevalent method for leaching gold, however it is pursued to be superseded due to environmental concerns and toxicity. Additionally, cyanide leaching is intended to limit or even forbid in various countries and states, preventing new plants to be established. (Laitos, 2012; Marsden & House, 2006) Possible alternative is halide leaching, which also possesses certain advantages over cyanide leaching. These include more flexibility due to controlling reagent dosages for enhancing dissolution rate of desired element, regeneration of specific oxidants, as well as halide leaching performs effectively for leaching gold in completely oxidized and certain refractory materials. Additionally, chloride media is more tolerant for leaching copper involved in gold ore or concentrate, while it increases chemical consumption in cyanide leaching. On the other hand, deficiencies include instability of gold halide complexes as they are tried to be retained in the solution. (Aylmore, 2005)

Before cyanidation, gold was leached with chlorination process, where chlorine gas was applied to the ore or concentrate. However, it was economically viable for high-grade ores only. (Rose, 1896) Chloride leaching of gold has been investigated for decades as an alternative, however, the development of gold chloride leaching is still ongoing and there is only little published research about batch leaching. Thus, the aim of this thesis was to display the potential in cupric chloride leaching of gold and to present a suitable alternative for cyanide in certain conditions. This is pursued by batch leaching parameter test series.

Theoretical part of this thesis includes a general introduction on gold dissolution in chloride media. Secondly, review of various leaching parameters affecting gold

dissolution in chloride media is rendered. These parameters include chloride concentration, oxidant and its concentration, pH, temperature and agitation. Thirdly, formation and stabilities of halide complexes (chloride, bromide and iodide) with gold are inspected and compared to those of cyanide. Then, previous cupric chloride batch leaching experiments and continuous leaching processes are reviewed. Finally, favorable raw materials for chloride leaching were investigated. Review is based on scientific articles and patents.

In the experimental part, different parameters and their correlations on gold dissolution are investigated. Cupric concentration (0.1–1 M), chloride concentration (1–5 M), temperature (50–95 °C), particle size, leaching duration (2–6 h) and circumferential speed (1–1.7 m/s) were studied with two different raw materials, which both were low-grade tailings. The hypothesis was that increasing chloride concentration, temperature, leaching duration and circumferential speed increase gold dissolution (von Bonsdorff, 2006; Lampinen, 2017), while increasing cupric concentration increases gold dissolution up till 0.6 M (McDonald, 1987). Decreasing particle size is also predicted to increase gold dissolution. Redox potential and pH were measured during the experiment to display the phenomena in the reactor. The focus was on gold extraction, however dissolution rates were also calculated from the results. Economic feasibility was not taken into account. In the current work, silver dissolution was also investigated.

2 Gold dissolution in chloride solution

It is common knowledge that gold dissolves as Au^+ and Au^{3+} (Marsden & House, 2006). By now, gold dissolution in chloride solution has been studied mainly with electrochemical measurements. Standard potentials of chloride complex reduction reactions for Au^+ and Au^{3+} are presented in Equations 1, 2 and 3. (Marsden & House, 2006) Electrochemical dissolution of gold occurs in acidic chloride solutions at oxidation potentials below 1.2 V vs. SHE (Standard hydrogen electrode) (corresponding 0.96 V vs. saturated calomel electrode (SCE)), forming both Au^+ and Au^{3+} species with $AuCl_2^-$ being the predominant species. At oxidation potentials above 1.2 V vs. SHE (corresponding 0.96 V vs. SCE), oxidation further into $AuCl_4^-$ is possible. (Nicol, 1980) At potential of 0.8 V vs. saturated calomel electrode (SCE) (1.044 V vs. SHE), gold dissolves as $AuCl_2^-$ with +1 oxidation state, while at higher potentials as $AuCl_4^-$ with +3 oxidation state (Diaz *et al.*, 1993). Frankenthal and Siconolfi (1982) agree that gold dissolves as Au^+ at potentials below 0.8 V vs. SCE (1.044 V vs. SHE), although they claim that Au^{3+} is more prevalent above 1.1 V vs. SCE (1.344 V vs. SHE).

$$AuCl_2^- + e^- \Leftrightarrow Au + 2Cl^- \qquad E^0 = 1.154\ V \qquad (1)$$

$$AuCl_4^- + 3e^- \Leftrightarrow Au + 4Cl^- \qquad E^0 = 0.998\ V \qquad (2)$$

$$AuCl_4^- + 2e^- \Leftrightarrow AuCl_2^- + 2Cl^- \qquad E^0 = 0.926\ V \qquad (3)$$

Dissolution of gold proceeds in two stages. During the first stage, aurous chloride intermediate is formed on the gold surface according to Equation 4. In the second stage, soluble $AuCl^-_2$ intermediate is formed. This is further oxidized to $AuCl^-_4$ or diffused into solution, depending on the potential. (Putnam, 1944)

$$Au + Cl^- \Leftrightarrow AuCl + e^- \qquad (4)$$

High oxidant requirements are typical for halogen processes (Aylmore, 2005). Therefore, diffusion of oxidants is usually rate-liming step, as chloride concentration is high in chloride systems (Jeffrey *et al.*, 2001). Although, von Bonsdorff (2007) and Lampinen *et al.* (2017) suggest that the reaction is under mixed control, meaning that charge transfer and mass transfer both affect the gold dissolution rate. Stability area of gold in chloride solution is presented in Figure 1. Contrary to indication of the diagram, oxygen is not strong enough oxidant to oxidize gold and form chloro-complex in the presence of chloride. To achieve this, stronger oxidants, such as chlorine, permanganate and

hypochlorite, are required. (Ferron *et al.*, 2003) Other important and oxidants are cupric and ferric ions (McDonald, 1987).

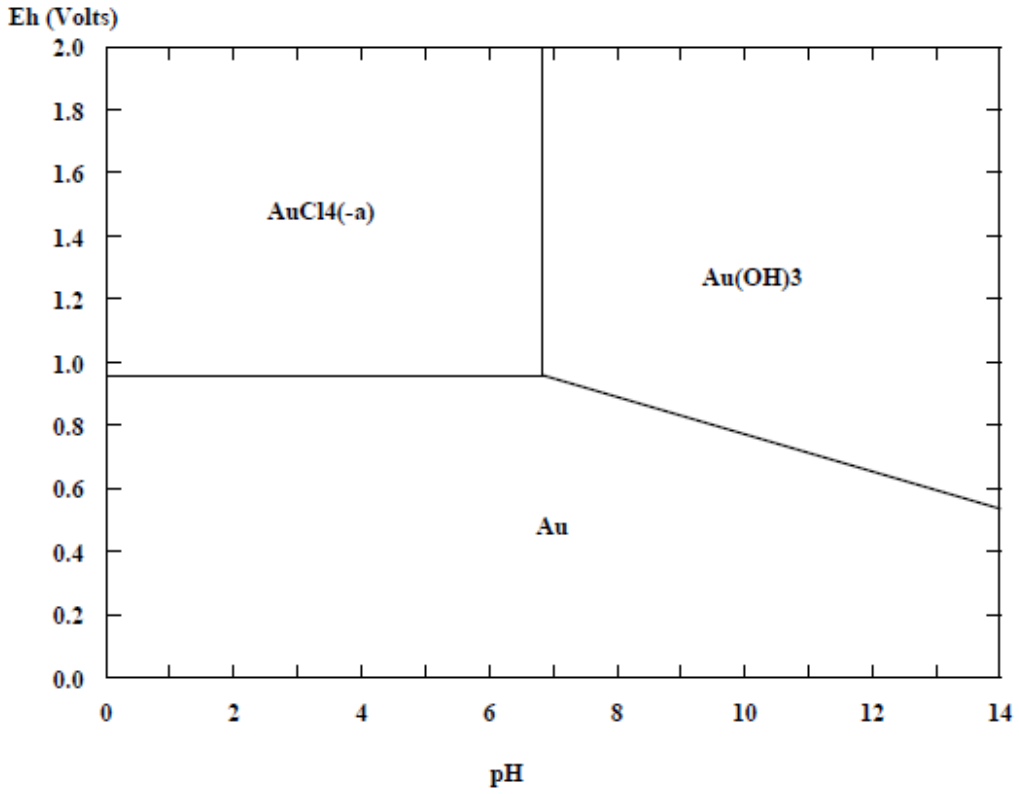


Figure 1. Eh – pH diagram for Au-Cl-H_2O system at 25 °C (Ferron *et al.*, 2003)

As depicted in Figure 2, most complexing agents used in gold leaching have small operating ranges compared to cyanide. According to Nicol (1980), high oxidizing potentials involved with some lixiviants lead to high reagent consumptions due to reaction with sulfide minerals and oxidation of the reagent itself. This is particularly typical for thiosulfate and thiocyanate, where consequently leaching conditions have to be better controlled than for cyanide leaching (Aylmore, 2005).

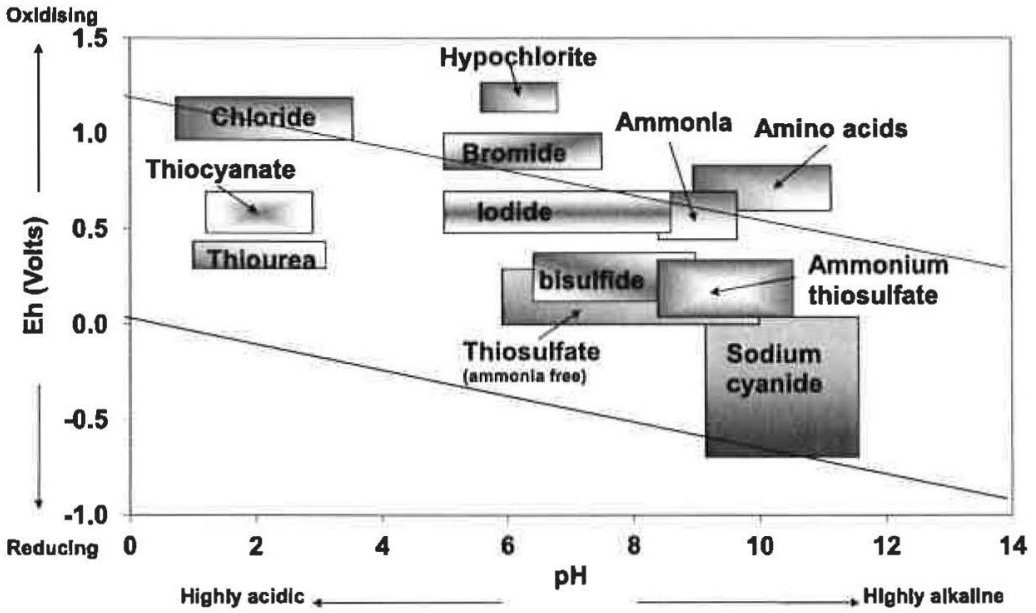


Figure 2. Typical gold lixiviant operating regions shown in Eh–pH diagram. (Aylmore, 2005)

Silver is generally associated with gold. This increases revenues from gold operations, although greater reactivity of silver influences the behavior of gold in flotation, leaching and recovery processes, which have to be taken into consideration when the silver grade is too high (>10 ppm). (Marsden & House, 2006) Pure silver dissolves faster than pure gold, however, presence of silver promotes dissolution of gold. Therefore, Ag(I) is suggested to catalyze gold dissolution by redox-displacement. (Senanayake, 2004) Nonetheless, chloride forms passivating film of insoluble silver chloride, when the silver content in the ore is high. This decreases the dissolution rate, thus high chloride concentration in solution is required to solubilize silver chloride. Consequently, chloride leaching is not ideal for ores with high silver contents. (Aylmore, 2005)

Significant setback for chloride leaching is preg-robbing. In this phenomenon, gold precipitates and/or adsorbs into the solids during leaching and it occurs in nearly all lixiviants. Generally, preg-robbing is associated with carbonaceous materials, such as natural carbon, hydrocarbons and organic acids, from which natural carbon is the most significant. These behave similarly to activated carbon, although they do not invariably result in poor gold recovery. (Ahtiainen & Lundström, 2016) Preg-robbing occurs with various mechanisms, which include gold reduction, physical adsorption and chemical adsorption (Miller *et al.*, 2005). Gold-chloro complexes also have a tendency to adsorb on mineral surfaces such as goethite, quartz and alumina (Baghalha, 2007).

Gold dissolution is reported as dissolution rate (mol/m^2/s). Due to prevalence of cyanide in gold industry, dissolution rates in chloride media are compared to dissolution rate of cyanide leaching. Typical dissolution rate of cyanidation is 1.29 mg/m^2/s (6.5 x 10^{-6} mol/m^2/s), which is achieved with cyanide concentration of 0.002 M CN^-. (Marsden & House, 2006). However, the cyanide concentration and dissolution rate are highly dependent on raw material. Gold dissolution rate can also be improved by adjusting process variables including temperature, oxidant concentration, pH and agitation.

3 Effect of Process Variables

Many process variables affect the dissolution rate of gold. In this thesis, temperature, oxidant and chloride concentration, pH and agitation are investigated in both theoretical and experimental part. Additionally, the effect of particle size and leaching duration are investigated in the experimental part.

3.1 Chloride Concentration

Chloride concentration has a strong effect on redox potential of cupric/cuprous couple in cupric chloride leaching system. Redox potential is increased as chloride concentration increases. McDonald *et al.* (1987) stated that increasing sodium chloride increases solubility of gold, while von Bonsdorff (2006 and 2007) claimed sodium chloride increases the dissolution rate of gold. Increasing sodium chloride concentration from 2.8 to 280 g/l, decreased corrosion potential by approximately -53 mV per decade and increased dissolution rate from 0.002 to 0.92 µm/h (from 5.44×10^{-8} to 2.50×10^{-5} mol/m^2/s) as presented in Figure 3. Abe & Hosaka (2010) claimed that suitable chloride concentration is from 1 to 6.5 M (from 35 to 230 g/l) and preferred from 3.3 to 5.2 M (from 118 to 186 g/l). As chloride concentration rose above 5.2 M (above 180 g/l), sodium chloride started to precipitate. Sodium chloride precipitation was also influenced by copper and iron chloride concentrations. When these concentrations rose, total chloride concentration increased too much and precipitated as sodium chloride crystal. Chloride ions are necessary to stabilize oxidants such as copper. It is especially important to stabilize cuprous ions and keep them in solution for regeneration to cupric ions. (Abe & Hosaka, 2010) Sodium chloride also affects the polarization resistance, which is likely due to dissolution occurring on the surface of the gold. In addition, chloride concentration affects the anodic reaction and complex formation in chloride systems. (von Bonsdorff, 2007)

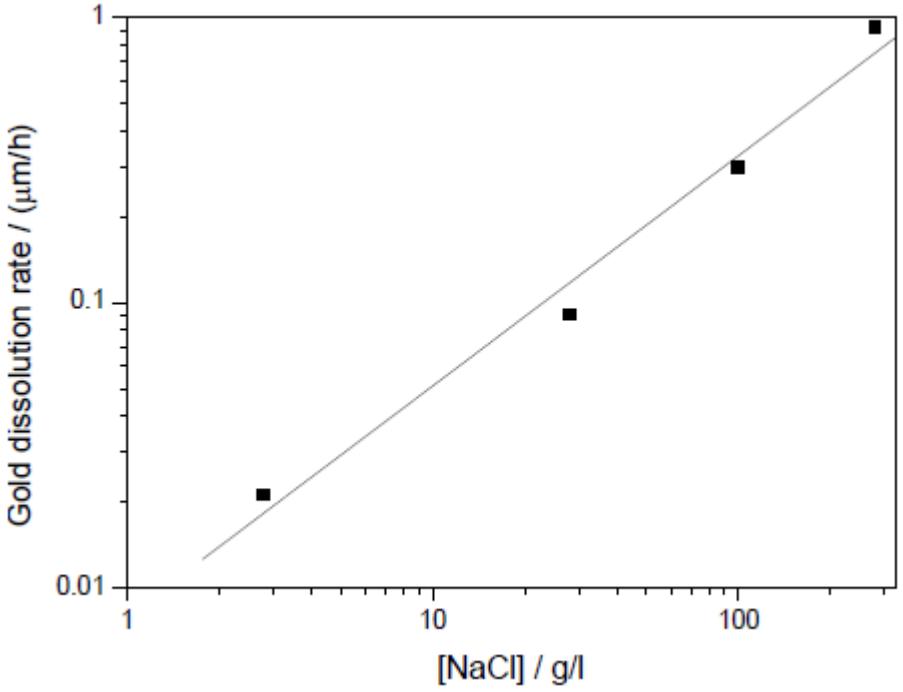


Figure 3. Gold dissolution rate as a function of NaCl concentration, when $[Cu^{2+}]$ = 30 g/l, T = 90 °C, pH = 2 and solution flow rate = 200 ml/min. (von Bonsdorff, 2007)

Current pilot projects usually operate with high chloride concentration and added bromide. Decrease on chloride concentration diminishes gold leaching kinetics, but on the other hand, high chloride concentrations increase operation costs by increasing wash water consumption, loss of chemicals to the bleed and leach residue as well as complicating process chemistry. (Lundström *et al.*, 2016b)

3.2 Oxidants

3.2.1 Cupric ion

Using cupric ions as oxidant in chloride leaching has been investigated in various conditions, although, aqueous cupric ion is seldom regarded as a strong oxidizing agent. Copper ion has two oxidation states; cuprous Cu(I) and cupric Cu(II). However, the hydrated cuprous ion is more unstable. Figure 4 a and b show copper chloride system in Eh-pH diagram in pH range of 0–5 and potential range of -2.00–2.00 V. Copper concentration is 0.5 M and chloride concentration is 1 M, whereas temperature is 25 °C in Figure 4 a and 95 °C in Figure 4 b. In 25 and 95 °C, copper is in elemental form when potential is under 0.1 V. When potential increases, copper occurs as cuprous ion, forming CuCl in 25 °C (0.12–0.52 V) and $CuCl_2^-$ in 95 °C (0.08–0.52 V). Cupric ions are more prevalent in potentials over 0.52 V, forming $CuCl^+$-complexes, and then occurring solely

as cupric ions in potentials over 1.20. When pH increases above 2.9 in 25 °C and 2.3 in 95 °C, copper forms hydroxides.

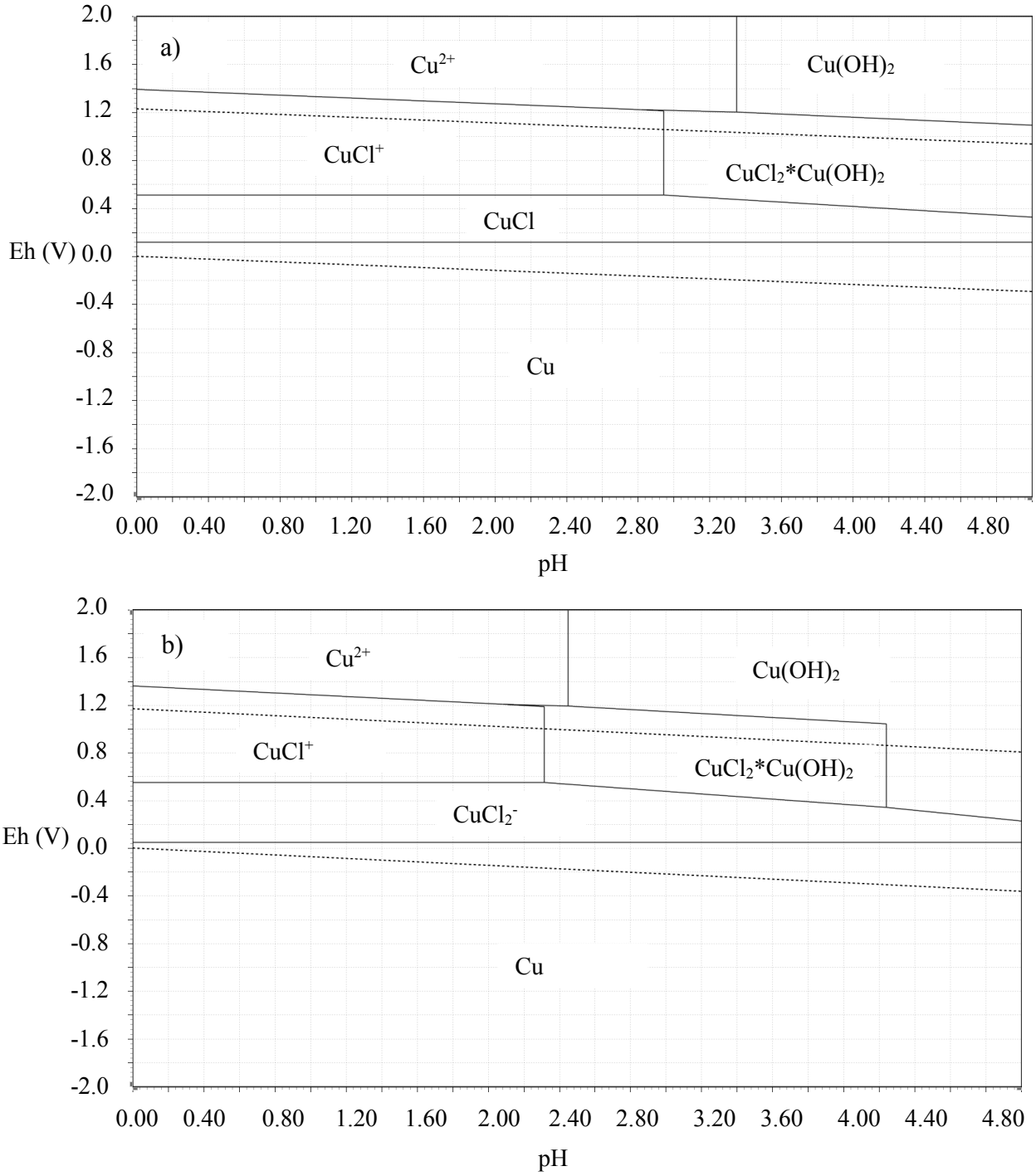


Figure 4. Copper chloride aqueous system potential-pH diagram in a) 25 °C and b) 95 °C, when [Cu] = 0.5 M and [Cl] = 1 M. Diagrams are achieved from Outotec's HSC 9.0 chemistry software.

Aurous and auric ions are highly instable, thus, their formation is limited. Yet, more stable complexation of ions moves the dissolution reactions 5 and 6 to the right. For example chlorides are such ions and their combined equations of oxidation and complexation are presented in Equations 7, 8 and 9. These equations generate equilibrium constants in

terms of the relative concentrations of uncomplexed products (Cu(I), Au^{+} and Au^{3+}) and reactants (Cu(II)). Uncomplexed products represent only little amount of total copper and gold in solution and have affinity for halide ligands. Additionally, the ratio of the cupric ion concentration compared to cuprous ion concentration affects the gold dissolution and gold solubility decreases with the increase in the cuprous ion concentration. (McDonald *et al.*, 1987) Copper chloro-complexation is presented in general Equation 10.

$$Cu^{2+} + Au \Leftrightarrow Cu^{+} + Au^{+} \qquad \Delta G^{\circ}_{298} = 157.3\ \mathrm{kJ/mol} \qquad (5)$$

$$3\ Cu^{2+} + Au \Leftrightarrow 3\ Cu^{+} + Au^{3+} \qquad \Delta G^{\circ}_{298} = 387.8\ \mathrm{kJ/mol} \qquad (6)$$

$$Au + 2Cl^{-} + Cu^{2+} \Leftrightarrow AuCl_2^{-} + Cu^{+} \qquad (7)$$

$$Au + 4Cl^{-} + 3\ Cu^{2+} \Leftrightarrow AuCl_4^{-} + 3\ Cu^{+} \qquad (8)$$

$$AuCl_2^{-} + 2Cl^{-} + 2\ Cu^{2+} \Leftrightarrow AuCl_4^{-} + 2\ Cu^{+} \qquad (9)$$

$$CuCl(s) + nCl^{-} \Leftrightarrow [CuCl_{n+1}]^{n-1} \qquad (10)$$

According to von Bonsdorff (2006), increasing cupric ion concentration increased corrosion potential, and also proportionally increased gold dissolution rate. However, gold dissolution was found to diminish, when cupric ion concentration was increased from 0.5 to 1 M (Lampinen *et al.*, 2017). McDonald (1987) suggested that the threshold, when effect of cupric ion concentration diminishes gold dissolution rate, is at 0.6 M and claimed that above this concentration, cuprous ion concentration rises too much limiting the process. Additionally, gold dissolves as aurous Au^{+} ion with cupric concentration below 0.1 M and as auric Au^{3+} ions at higher concentrations. According to Haavanlammi *et al.* (2010), in Hydrocopper™ process, cupric concentration is suggested to be 40-100 g/l (0.6-1.5 M), differing from the results of Lampinen *et al.* (2017) and McDonald (1987). However, it should be noted that in Hydrocopper™, mineralogical structure of the sulfide ores need to be oxidized, where higher cupric concentration is also required. The effect of cupric chloride on gold dissolution is shown in Figure 5.

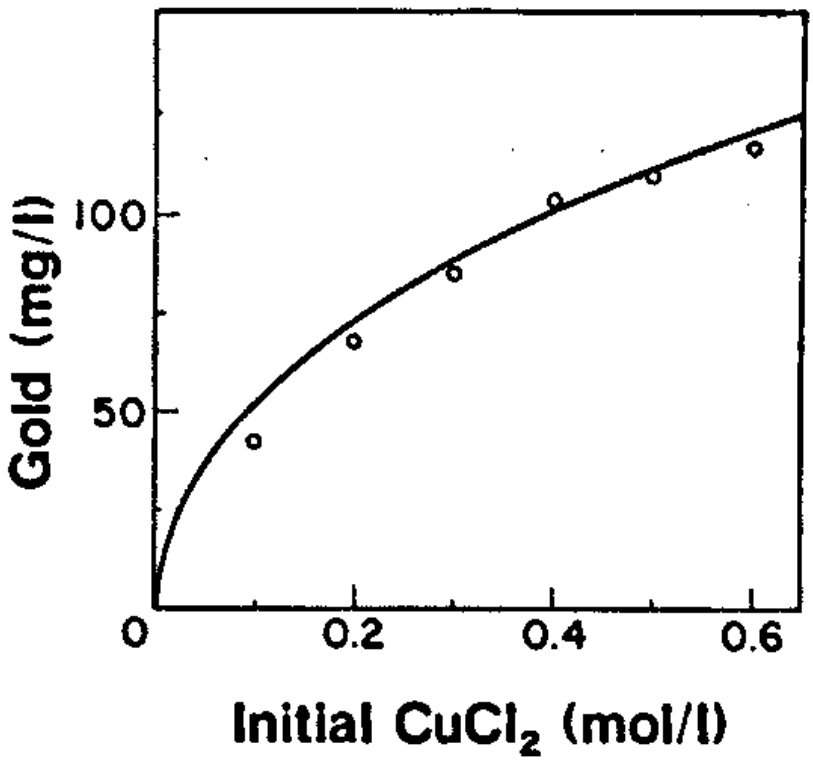


Figure 5. Gold dissolution as a function of initial cupric chloride in solution, when *T* = 102 °C, *[NaCl]* = 3.42 M and [HCl] = 0.1 M. (McDonald *et al.*, 1987)

Oxidative power of solution can be restored with oxygen by regenerating oxidants, such as cuprous ions to cupric species illustrated in Equation 11. (McDonald *et al.*, 1987) Nonetheless, excessive oxidation and increase in pH value can result in precipitation of copper hydroxyl chloride, therefore, copper losses in the leach residue (Equation 12) (Hyvärinen & Hämäläinen, 2005). Oxygen allows the oxidation-reduction potential to be increased to 600-650 mV vs. Ag/AgCl (555-605 mV vs. SCE), which is suitable for gold leaching (Haavanlammi *et al.*, 2010).

$$2\,Cu^{+} + ½O_2 + 2H^{+} \Rightarrow 2Cu^{2+} + H_2O \quad (11)$$

$$2\,Cu^{+} + 3OH^{-} + Cl^{-} \Rightarrow Cu_2(OH)_3Cl \quad (12)$$

3.2.2 Ferric ion

Ferric ions are another potential oxidant for gold leaching in chloride system. Ferric ion concentration proportionally increases gold dissolution rate up to 0.5 M, resulting in only slight increase in dissolution rate at 0.75 M and none at 1 M ferric ion concentration. (Seisko *et al.*, 2018) This is demonstrated in Figure 6 as remaining gold grade in leach residue as function of iron concentration in leaching solution (Abe *et al.*, 2013).

According to Abe and Hosaka (2010), the optimal ferric ion concentration for chloride leaching is 0.01–0.26 g/l (0.0002–0.0047 M). However, Lundström *et al.* (2016b) suggested that ferric ion concentration of 9-20 g/l (0.16–0.36 M) is more advantageous.

Gold dissolution in ferric chloride solution is presented in Equation 13 and further oxidation in Equation 14. Similar to cupric chloride process, ferric chloride process requires oxygen to regenerate reduced ferrous ions back to ferric ions. This reaction is shown in Equation 15. (Liu & Nicol, 2002)

$$Au + 2Cl^- + Fe^{3+} \Leftrightarrow AuCl_2^- + Fe^{2+} \quad (13)$$

$$AuCl_2^- + 2Cl^- + 2Fe^{3+} \Leftrightarrow AuCl_4^- + 2Fe^{2+} \quad (14)$$

$$O_2 + 4H^+ + 2Fe^{2+} \Rightarrow 2H_2O + 2Fe^{3+} \quad (15)$$

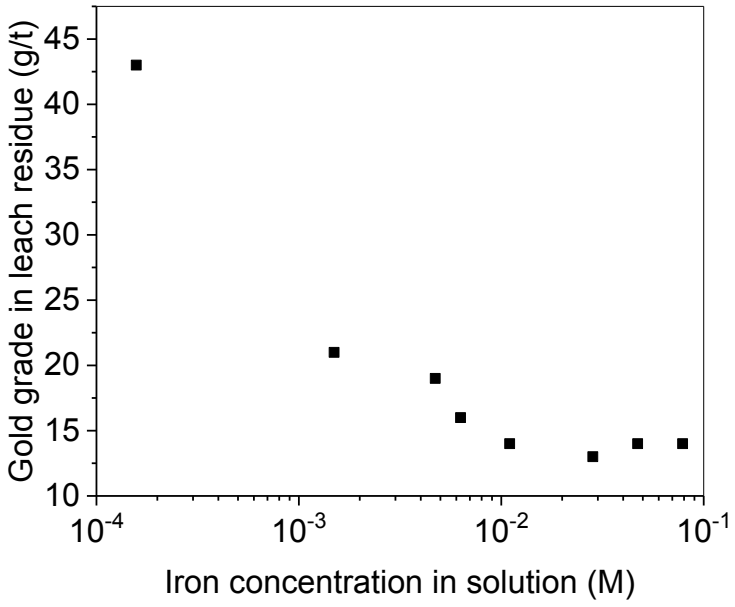
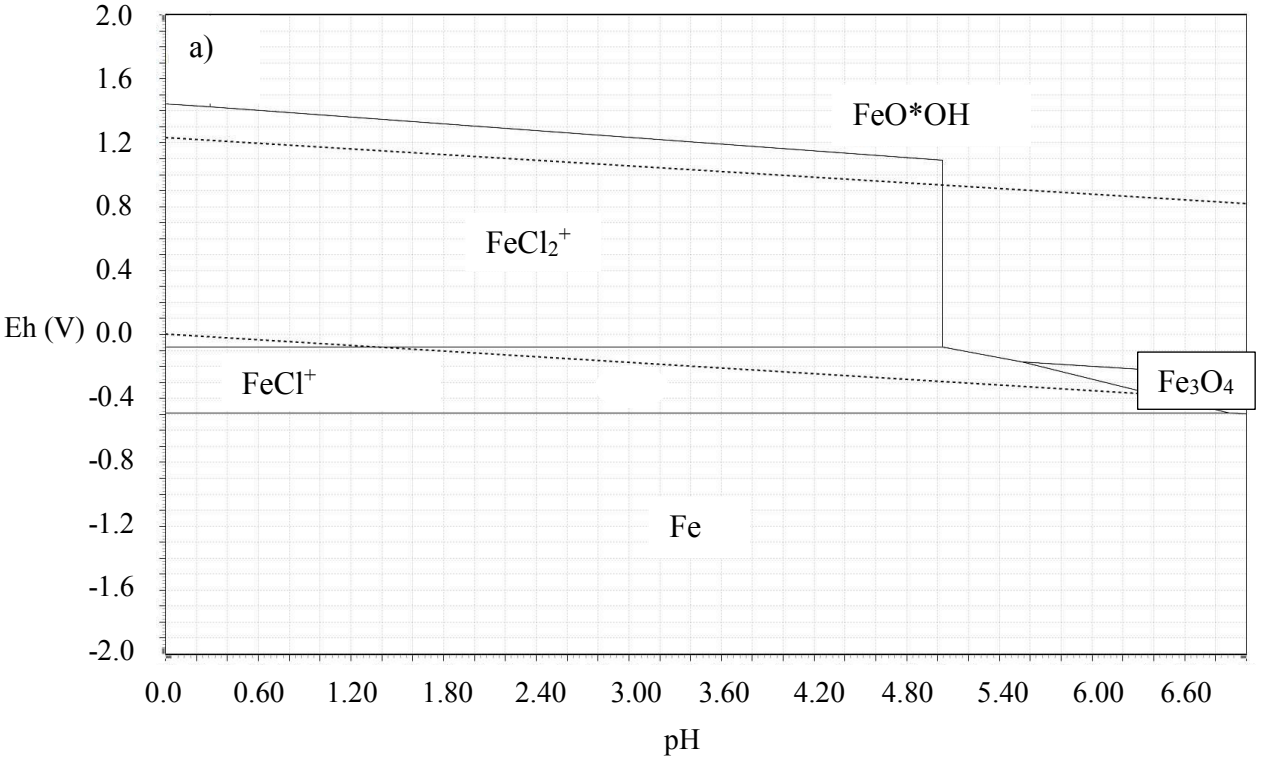


Figure 6. Impact of iron concentration on gold leaching with 50 g/t gold grade ore. Modified after Abe *et al.* (2013).

Ferric ions exist in chloride solutions in ionic form or as chloro-complexes, such as $FeCl^{2+}$, $FeCl_2^+$ and $FeCl_3$(aq) (Muir, 2002). Increasing chloride concentration, increases $FeCl^{2+}$, $FeCl_2^+$, $Fe(H_2O)Cl^{2+}$ and $FeCl_3$(aq) concentrations, while reducing Fe^{3+} concentration. Fe^{3+} species are predominant within chloride concentration of 0-2 M, $FeCl^{2+}$ within 2-5 M and $FeCl_3$ above 5 M. (Strahm *et al.*, 1979) In order to maintain ferric ions in solution, low pH is required. As pH decreases, iron solubility increases and furthermore, when pH rises above 1.9, iron precipitates as hydroxides. Therefore, pH must be below 1.9 for iron to be soluble and oxidant in ferric-chloride gold process. (Abe

& Hosaka, 2010) Seisko *et al*. (2018) argues the threshold for precipitation is pH of 1.5 at 95 °C with $[Fe^{3+}]$ = 0.5 M. Figure 7 a and b display iron chloride system in Eh-pH diagram in pH range of 0–7 and potential range of -2.00–2.00 V. Iron concentration is 0.2 M and chloride concentration is 1 M, whereas temperature is 25 °C in Figure 4 a and 95 °C in Figure 4 b. Iron occurs as elemental iron in potential below -0.50 V at 25 and 95 °C and forms oxides when pH increases. In 25 °C, the prevailing form of iron is FeO*OH when pH increases above 5 and in 95 °C as Fe_2O_3 when pH increases above 4, indicating the pH threshold is higher than in the studies of Abe & Hosaka (2010) and Seisko *et al.* (2018).



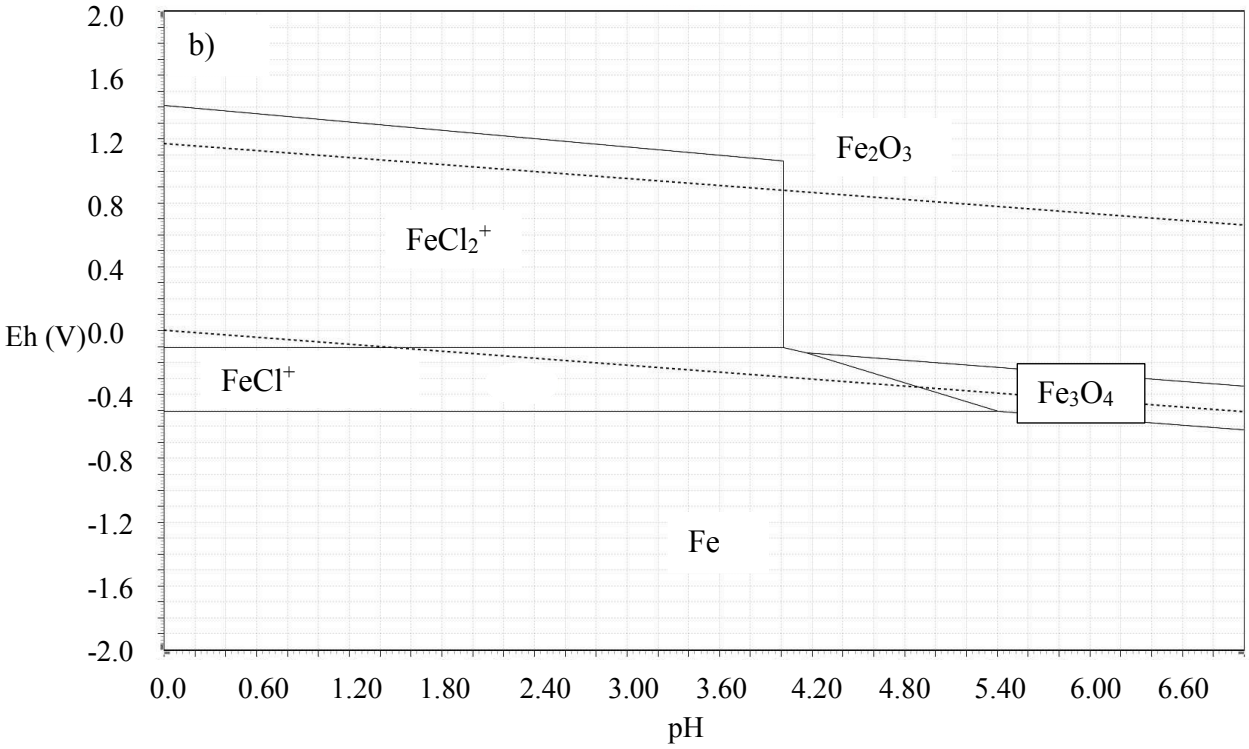


Figure 7. Iron chloride aqueous system potential-pH diagram in a) 25 °C and b) 95 °C, when [Fe] = 0.2 M and [Cl] = 1 M. Diagrams are achieved from Outotec's HSC 9.0 chemistry software.

3.2.3 Chlorine

Chlorine was used in gold operations as an oxidant in the past before cyanidation (Liu & Nicol, 2002). Gold dissolution rate in chlorine-chloride system is more rapid than that by cyanide. However, chlorine is highly oxidative and reacts vigorously with sulfide and gangue carbonate minerals, thus only high-grade materials may be treated economically. (Baghalha, 2007) Halide gases are expensive, highly corrosive and hazardous to utilize and store. Furthermore, halide gases tend to generate high redox potentials, and excessive amounts cause passivation of raw material. (Abe & Hosaka, 2010). According to Jeffrey *et al.* (2001), oxy-chloride species, such as hypochlorous acid and hypochlorite, can be used as oxidants for gold chloride system. Equation 16 shows the cathodic reduction of chlorine. Equation 17 presents the reaction of gold dissolution from elemental gold to gold(III)-chloro complex in chloride system, provided the pH is less than 2 (Finkelstein *et al.*, 1966).

$$Cl_2 + 2e^- \Rightarrow 2Cl^- \qquad E^0=1.40\ V \qquad (16)$$

$$2\,Au + Cl_2 + 2Cl^- \Leftrightarrow [AuCl_4]^- \qquad (17)$$

3.3 pH

The pH in chloride media is mainly dependent on the used oxidant as overly high pH causes oxidants (copper and iron) to precipitate (von Bonsdorff, 2007; Seisko *et al.*, 2018). Jeffrey *et al.* (2001) argues, that effectiveness of gold leaching in chloride media depends highly on pH level as kinetics improve, when pH lowers. However, the experiments were performed in pH levels, where oxidants such as cupric and ferric ions precipitate. Stability of gold chloride complexes is also noted to be influenced by the solution pH (Aylmore, 2005). Still, von Bonsdorff (2007) argues that the effect is noted to be insignificant in cupric chloride media, as long as the solution pH is <3 and the main impact is towards the cupric ions. In the process with pH <3, cupric ion precipitation to atacamite, $Cu_2(OH)_3Cl$, did not occur. Figure 8 demonstrates that acidic environment is preferred for gold dissolution in chloride media. As presented in Equations 11 and 15, oxidative reaction also consumes hydrogen ions, therefore, acid is also required. This will further increase the oxidation potential, meaning that combination of hydrogen ions and oxygen environment is conductive to gold dissolution in cupric chloride system. (McDonald, 1987) However, at lower pH, impurity level increases, causing chloride ions to form complexes with impurities, resulting in larger amounts of bleed in process. HCl concentration in process is suggested to be below 40 g/l. (Lundström *et al.*, 2016b)

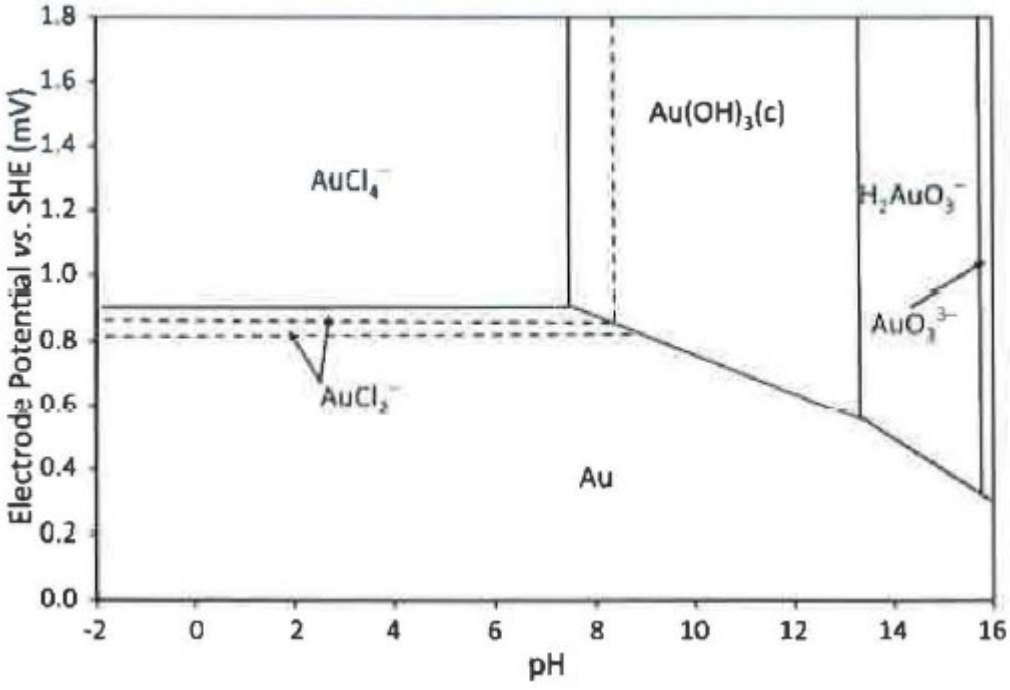


Figure 8. Au-Cl-H_2O system potential vs. pH diagram at T = 298 K (Adams, 2016a).

3.4 Temperature

Temperature reduces polarization resistance and increases gold dissolution rate (von Bonsdorff *et al.*, 2005). Figure 9 displays the effect of temperature in temperature range of 80–85 °C and the effect is increasing linearly from 80 to 90 °C. Gold dissolution rate remains stale when increased from 90 to 95 °C, with cupric concentration of 15 and 20 g/l (0.24 and 0.31 M), however, with cupric concentration of 30 g/l (0.47 M), dissolution rate increases further. According to Lampinen *et al.* (2017), the most significant change in gold dissolution rate occurred, when temperature was increased from 65 to 75 °C. Furthermore, increasing temperature from 90 °C to 100 °C has been found to double the solubility of gold in solution. Logarithmical gold concentration as the function of the inverse of temperature is presented in Figure 10. (McDonald, 1987)

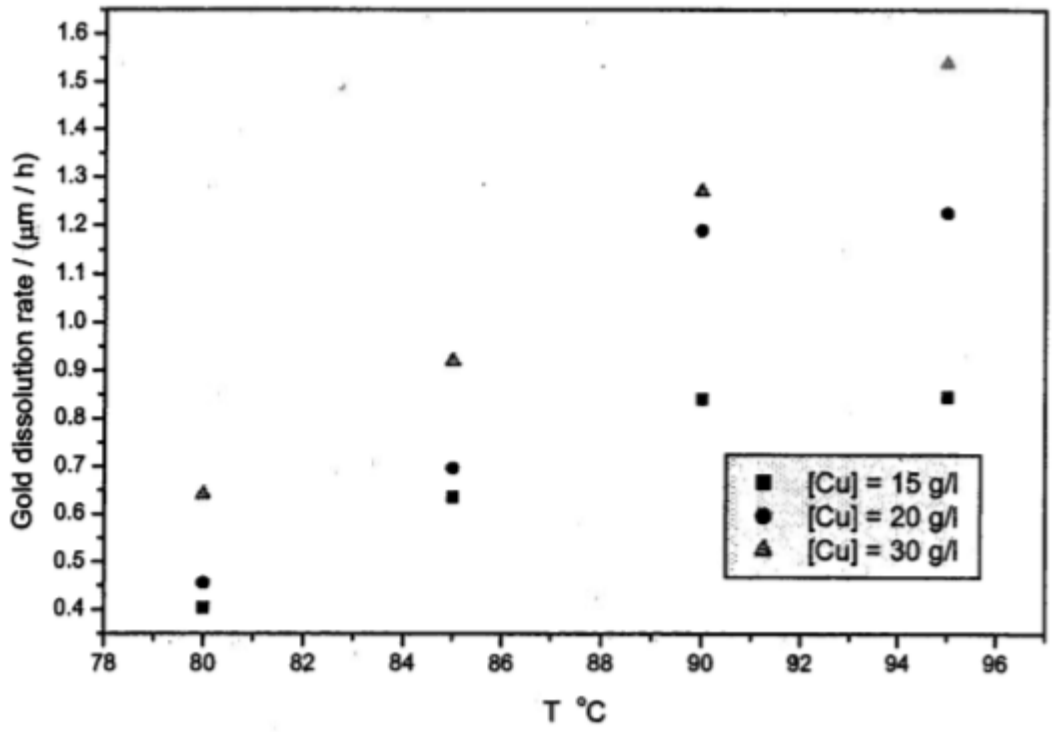


Figure 9. Effect of temperature on gold dissolution rate. *[NaCl]* = 280 g/l, *[Cu^{2+}]* =15–30 g/l, T = 80–95 °C, *pH* = 2.

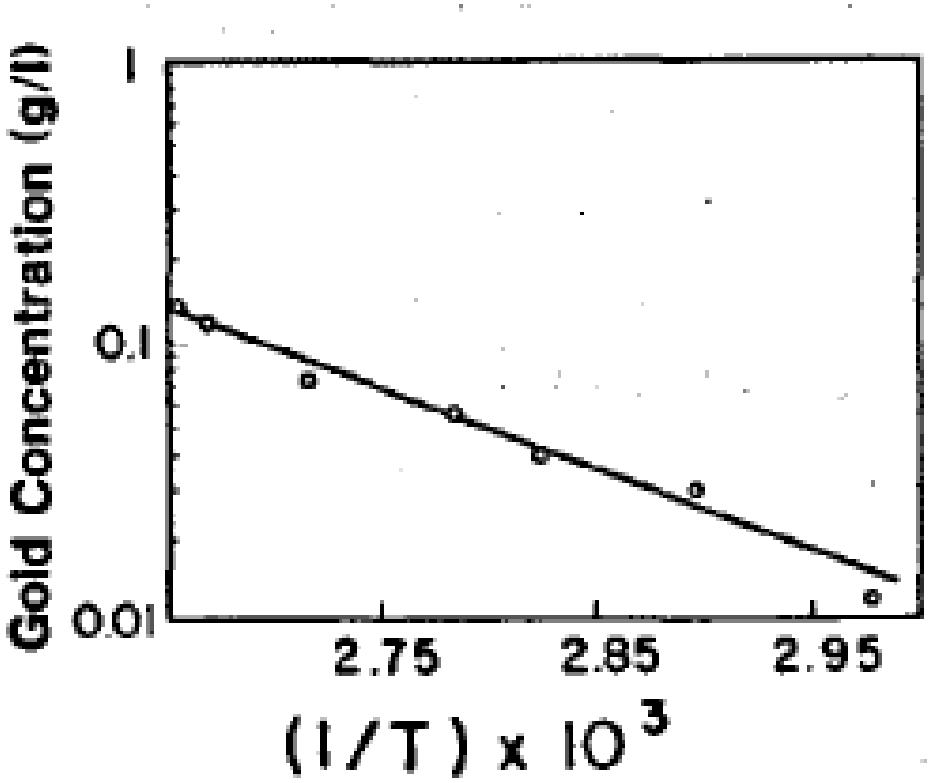


Figure 10. Solubility of gold as a function of temperature, when *[NaCl]* = 3.42 M, *[$CuCl_2$]* = 0.6 M, and [HCl] = 0.1 M (McDonald, 1987).

3.5 Agitation

Rotational speed increases mass transfer, thus, increasing gold dissolution rate. At low rotational speed and low oxidant concentration, the dissolution is mainly controlled by mass-transfer. However, at higher rotational speed, generated mass-transfer cannot be maintained if oxidant concentration was too low in the solution. Increasing rotational speed thins diffusion layer and mass-transfer is no longer the limiting factor. This increases gold dissolution rate, however, at high rotational speed dissolution rate evens, when diffusion layer is thinned and reaction is controlled by charge-transfer. (Lampinen *et al.*, 2017)

4 Raw material

The most common form of gold mineral is native gold. However, ore grades are depleting and becoming increasingly more difficult to process. La Brooy *et al.* (1994) classify gold ores and concentrates into free-milling gold ores, from which above 90% is extracted in cyanide leaching, complex gold ores that consume large amounts of reagents and refractory gold ores as all remaining ores with low recovery. Refractory ores can either be silicates and oxides physically locking gold, chemically locking as gold compounds or reactive gangue mineralogy containing leach robbing minerals and preg-robbing materials. This has caused more emphasis on refractory gold ore pretreatment. Because of the diversity, there is no distinct treatment for refractory ores and every specimen has to be evaluated individually. (Pangum & Browner, 1996) Concentrates of refractory ores are generally low grade and contain harmful elements such as lead, antimony and arsenic (Adams *et al.*, 2015). These may cause the concentrates untreatable or uneconomic to process and therefore, oxidative pretreatment is used for sulfide, carbonaceous and telluride ores and concentrates to increase the gold extraction. The oxidation methods are divided into hydrometallurgical and pyrometallurgical methods. Pyrometallurgical oxidation mainly comprises roasting of sulfide and carbonaceous ores, however increasingly strict legislation of roaster emissions has increased the complexity and cost of roasting processes. Therefore, new hydrometallurgical methods are pursued, in addition to pre-aeration techniques. (Marsden & House, 2006)

4.1 Sulfides

Reductive nature of sulfide materials enhances the instability of gold-chloride complexes, causing chloride system to be poor for leaching gold from certain sulfide materials. Additionally, base metal sulfides are oxidized in chloride media, resulting in elemental sulfur formation near pH of 1.5 (Lundström *et al.*, 2008; Lundström *et al.*, 2009). This may cause layers, which avert gold dissolution (Abe & Hosaka, 2010). Nonetheless, reducing the reactivity of sulfides in halide systems has been investigated. Flotation collectors have been used to coat sulfides, reducing their reactivity without diminishing the gold dissolution rate. This method had success for some metal sulfides, such as copper sulfides, but for other sulfides such as pyrite, the attempts were unsuccessful. (Aylmore, 2005) Pyrite and arsenopyrite are common iron minerals associated with gold. These are refractory, yet heavy oxidation can be used to liberate the gold. Equation 18 depicts the destruction of lattice and, thus, the liberation of gold from pyrite and Equation 19 from

arsenopyrite. Such oxidation has been experimented successfully in Intec Gold Process, where pyrite, pyrrhotite, chalcopyrite and stibnite have been treated suitably. (Intec Ltd., 2009) According to Dreisinger (2016), cupric and ferric chlorides are suitable for oxidizing sulfide minerals in oxidative leaching.

$$FeS + 15O_2 + 2H_2O \Rightarrow 8SO_4^{2-} + 4Fe^{3+} + 4H^+ \quad (18)$$

$$FeAsS + 2O_2 \Rightarrow FeAsO_4 + S \quad (19)$$

Copper sulfide ores and silicate ores accompanied with copper sulfide ores are common gold sources. Methods for recovering the gold from aforementioned ores are divided into pyrometallurgical and hydrometallurgical. The pyrometallurgical method involves high temperatures, typically 1000 °C or more, where gold is achieved as byproduct from copper smelters. The hydrometallurgical method involves leaching the copper sulfide in a solution with complex-forming compounds and oxidants, dissolving the gold. This is later recovered by adsorbing on the surface of activated carbon. Hindrance in this method are present metals in concentrate, such as copper and iron, which form complex compounds, thus wasting complex-forming agents. Therefore, it is suggested to remove metals to sufficient levels beforehand. (Abe & Hosaka, 2010) Current cyanide leaching methods require large amounts of cyanide to leach refractory sulfide ores. Therefore, these ores are pretreated, to completely oxidize the refractory part of the ore. Ore oxidation may form phases in the rock, which have high solubility in cyanide leaching. This increases cyanide consumption and interfere with processing, rendering current cyanide leaching methods unsuitable for refractory sulfide materials. (Marsden & House, 2006)

Chalcopyrite is important copper mineral, however, it dissolves slowly (Hyvärinen & Hämäläinen, 2005). Chloride leaching is a possible treatment for chalcopyrite due to the aggressive nature of the leaching and to the stability of copper-chloro complexes. Leaching chalcopyrite in cupric chloride media, $[Cu^{2+}] < 9$ g/l (0.14 M) was noted to have no effect on the reaction rate and the reaction rate control appeared to change at that point also. With higher cupric ion concentrations, the control is observed to be diffusion of cupric ions through the reaction product layer, whereas with lower concentrations the reaction was under chemical or mixed control. (Lundström, 2005) In acidic environment under oxidation, chalcopyrite will first turn into bornite, then chalcocite, covellite and ultimately copper ions in solution. Therefore, it is possible to leach chalcopyrite and liberate gold within the lattice. Main reaction for chalcopyrite leaching is shown in

Equation 20. (Dreisinger, 2016) According to Yoshimura & Takebayashi (2016), N-ChlO process by JX Nippon Mining & Metals is effective halide leaching method for leaching copper from chalcopyrite and other sulfide ores. In the process, gold is also recovered sequentially. Hydrocopper™ method is similar. Copper in sulfide materials is the main product and gold containing waste or intermediate can be leached afterwards in halide media. (Haavanlammi *et al.*, 2010) Chalcopyrite can be dissolved in water below boiling point using cupric ions as oxidant. While leaching copper in copper chloride media, stability of cuprous ions is beneficial. Copper is oxidized to lower oxidation states as opposed to sulfuric acid leaching, thus, saving energy. (Hyvärinen & Hämäläinen, 2005)

$$CuFeS_2 + 0.5Cl_2 + 0.75O_2 + NaCl + 0.5H_2O \rightarrow NaCuCl_2 + FeO(OH) + S \qquad (20)$$

4.2 Polymetallic

Alongside refractory ores, polymetallic ores are processed constantly more, as free-milling and oxide ores are depleting (Adams, 2016b). Polymetallic orebodies contain various valuable metals at low grades. These include precious metals such as gold, silver and platinum group metals, other valuable metals such as cobalt, nickel and copper as well as rare-earth metals. (Adams *et al.*, 2015)

It is common for gold to occur in commercially viable copper ore. Gold grade in ore could be too low for mining the ore only for the gold content, however, it has added value alongside the copper content. (Sceresini & Breuer, 2005) Adams *et al.* (2015) investigated gold and silver extraction of polymetallic copper-gold concentrates in chloride media, resulting in above 90% gold and silver extraction. In comparison to cyanidation, the results were 8% and 0%, respectively.

Considerable amount of gold is recovered as a byproduct of base metal production. In 2004, around 10% of gold production was from byproducts. Although majority was recovered from the copper industry, large amounts were also recovered as a byproduct from nickel and lead industry. Additionally, possibilities lie within zinc and cobalt industry. Chloride leaching opens up opportunities in polymetallic ore leaching. Ferric chloride leaching is capable method for extraction of lead, silver and gold. Platsol™ Process introduces a chloride-assisted pressure leaching process, with approximately 90% extraction rates for copper, nickel, cobalt, palladium, platinum and gold. Among polymetallic ores, which contain low grades of various valuable metals, chloride leaching is a promising method. (Ferron, 2016)

4.3 Tailings

Tailings comprise of materials, which are non-profitable leftovers from gold extraction processes. These processes include cyanidation, flotation, gravity concentration and amalgamation. As waste, tailings are exceedingly diverse and depend on the original ore, original extraction process and its efficiency as well as the age of tailings deposition. Dominance of cyanidation in gold leaching results in cyanidation tailings, with gold components commonly being refractory. Therefore, cyanidation is mainly inefficient in gold extractions from tailings, resulting in recovery of 40% to 70%. Gold in cyanidation tailings typically occur as free or exposed gold from partial leaching of coarse gold particles, locked within silicate, oxide or sulfide gangue or free gold coated during dissolution and precipitation reactions. (Marsden & House, 2006)

5 Halide complex stability

The low stability of halide gold complexes is one of the defects for halide leaching, unlike gold cyanide complexes, which are very stable and difficult to decompose. Halide gold complexes are dependent on the solution pH value, composition, solution potential and presence of reductants in the ore, such as sulfidic minerals and metals. Residual amount of oxidant maintains a high solution potential for avoiding precipitation of metallic gold from solution. Order of the halide stability, beginning from the most stable, is iodide, bromide and chloride. In turn, the reaction rate is the opposite as chloride system has the highest dissolution rate, followed by bromide and finally iodide. (Aylmore, 2005) There is, however, discrepancy and in more recent studies Hojo *et al.* (2015) have noticed more rapid dissolution rate with bromides than with chlorides. Yet, halide leaching is considerably more rapid than cyanide leaching. (Aylmore, 2005)

Halide and cyanide species that form stable gold complexes are listed in Table 1. Stability is described with sign β and logarithmic scale is used for more apprehensible comparison. Cyanide is significantly more stable than halide complexes. Some complexing ligands form more stable complexes with Au^{+} and others with Au^{3+}. This preferred oxidation state is determined by electron configuration of the donor ligand. Ligands are divided into soft and hard electron donor ligands. The aforementioned include ligands such as cyanide and thiosulfate, which prefer metal ions of low valency, whereas the latter, like halides, prefer high-valency metal ions. (Marsen & House, 2006)

Table 1. Stability constants for halide and cyanide Au^{+} and Au^{3+} complexes at 25 °C. Modified after Senanayake (2004).

Ligand	Complex	log β
Chloride	$AuCl^{-}_{2}$	9.71
	$AuCl^{-}_{4}$	25.3
Bromide	$AuBr^{-}_{2}$	12.7
	$AuBr^{-}_{4}$	32.8
Iodide	AuI^{-}_{2}	19.2
	AuI^{-}_{4}	47.7
Cyanide	$Au(CN)^{-}_{2}$	38.3
	$Au(CN)^{-}_{4}$	85

Various ligands' standard reduction potentials are shown in Figure 11 and whether they rather form complexes with Au^{+} or Au^{3+}. Points above diagonal line comprise of ligands, which generally form complexes with Au^{+}, whereas ligands below the diagonal line rather

form complexes with Au^{3+}. Comparison of the corresponding potentials for reducing oxidized ligands are also included in the figure. (Nicol, 1980)

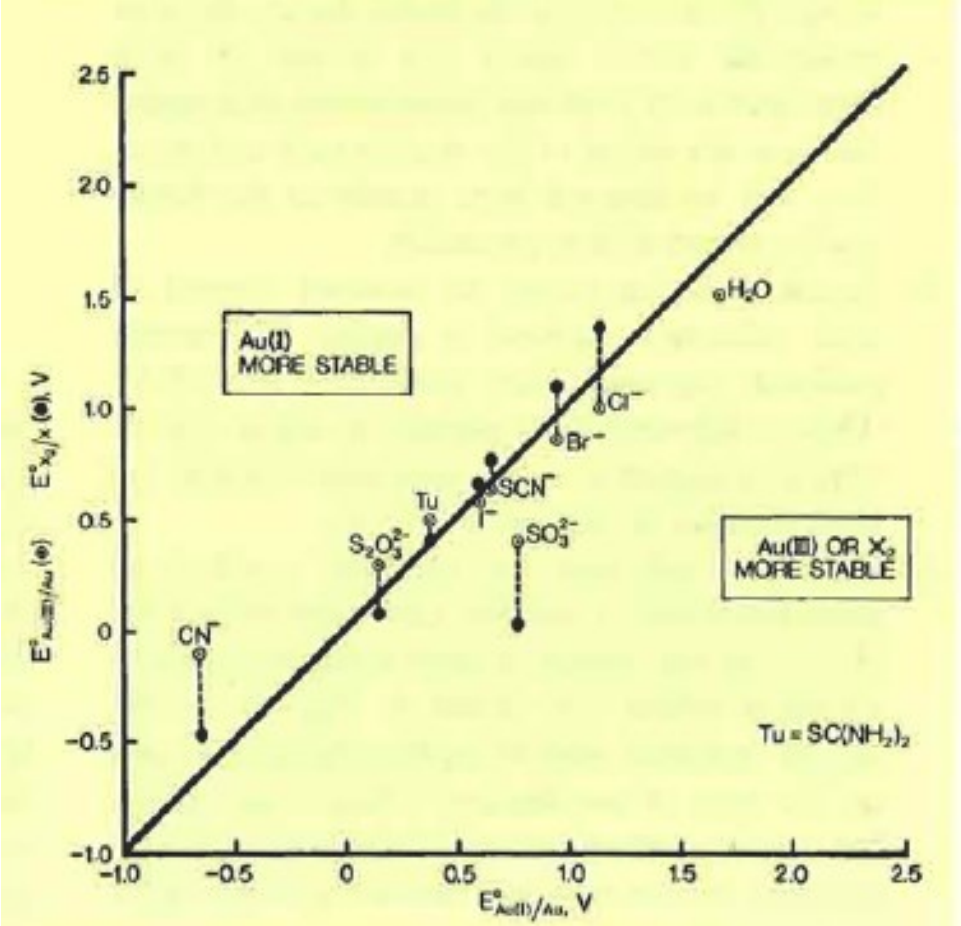


Figure 11. Standard reduction potentials of Au^{+} and Au^{3+} complexes (Nicol, 1980).

Figure 12 describes the chemistry of predominant oxidation states of gold in solution without stabilizing ligands. Thence it can be seen that the stability regions for the un-complexed Au^{+} and Au^{3+} are insignificant. Furthermore, there is no stability region for Au^{+}-oxides. (Nicol, 1980)

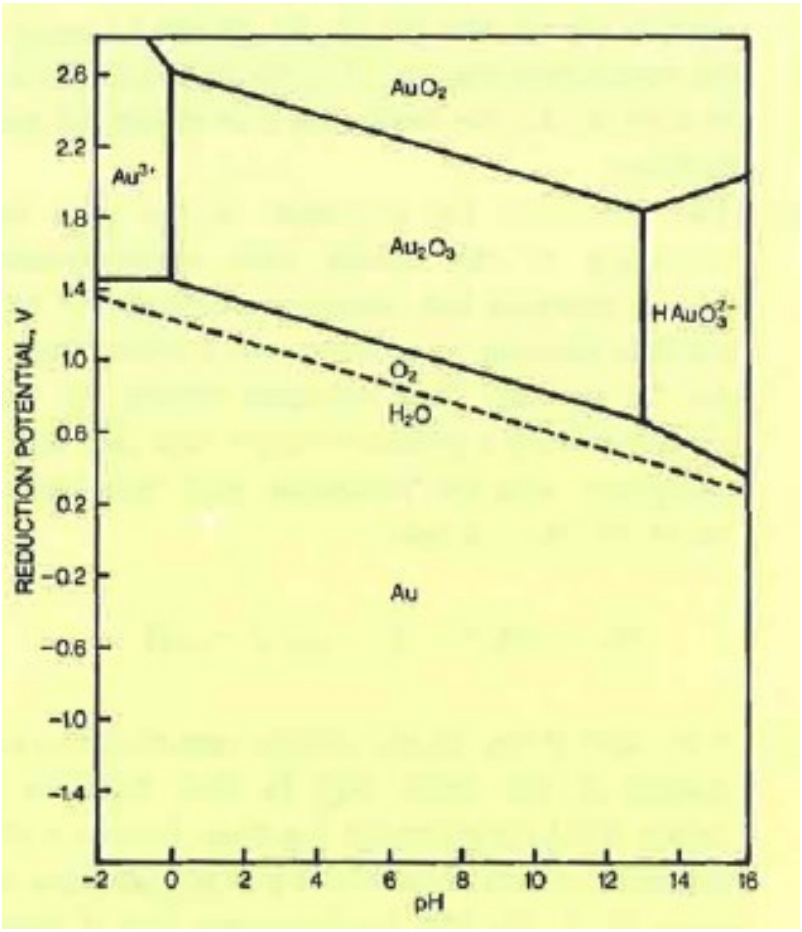


Figure 12. Pourbaix diagram for gold in aqueous solution at 25 °C (Nicol, 1980).

5.1 Chloride

As mentioned before, gold-chloride-water systems comprises $AuCl_2^-$ and $AuCl_4^-$ ions, from which $AuCl_4^-$ is more stable due to lower standard electrode potential. $AuCl_2^-$ ions are noted to be stable only at low gold concentrations and high chloride concentrations, as seen in Equation 21, however, the occurrence of mentioned disproportion reaction is very controversial. $AuCl_4^-$ reduction reaction is depicted in Equation 22. (Diaz *et al.*, 1993) According to Muir (2002), increasing Cl^- activity also increases $AuCl_2^-$ stability with respect to $AuCl_4^-$. Geometry of gold-chloride complexes vary as $AuCl_2^-$ is linear and $AuCl_4^-$ is square planar (Pan 1993).

$$3\,AuCl_2^- \Leftrightarrow AuCl_4^- + 2\,Au + 2Cl^- \quad (21)$$

$$AuCl_4^- + 2e^- \Leftrightarrow AuCl_2^- + 2Cl^- \quad (22)$$

Table 2 presents formation constants for different gold and copper complexes in chloride media. It can be seen that temperature increases the stability of mentioned chloro-

complexes. At 102 °C, near process temperatures, gold preferably forms $AuCl_4^-$ complexes, while cupric ions form $CuCl^+$, $CuCl_2$, $CuCl_3^-$ and $CuCl_4^-$; and cuprous ions form $CuCl_2^-$ and $CuCl_3^{2-}$. High chloride concentration furthers silver chloride dissolution and improves the stability of chloride complexes of other noble metals (Kononova *et al.*, 2014).

Table 2. Formation constants for gold and copper species in aqueous solutions (McDonald *et al.*, 1987).

Formation constant	Value at 25 °C	Value at 102 °C	Reference
$K=[AuCl_2^-][Cu^+]/[Cu^{2+}][Cl^-]^2$	1.4×10^{-17} M^{-1}	9.4×10^{-13} M^{-1}	Wagman *et al.*, 1982
$K=[AuCl_4^-][Cu^+]^3/[Cu^{2+}]^3[Cl^-]^4$	2.1×10^{-43} M^{-3}	3.5×10^{-30} M^{-3}	Wagman *et al.*, 1982
$\beta=[AuCl_2^-]/[Au^+][Cl^-]^2$	5.1×10^{10} M^{-2}	7.1×10^{9} M^{-2}	Pouradier *et al.*, 1965
$\beta=[AuCl_4^-]/[Au^{3+}][Cl^-]^4$	1.9×10^{25} M^{-4}	3.3×10^{24} M^{-4}	Wagman *et al.*, 1982
$\beta=[CuCl_2^-]/[Cu^+][Cl^-]^2$	6.9×10^{5} M^{-2}	9.6×10^{5} M^{-2}	Vasil'ev *et al.*, 1975
$\beta=[CuCl_3^{2-}]/[Cu^+][Cl^-]^3$	9.1×10^{5} M^{-3}	4.9×10^{5} M^{-3}	Vasil'ev *et al.*, 1975
$\beta=[CuCl^+]/[Cu^{2+}][Cl^-]$	4.0 M^{-1}	16.7 M^{-1}	Khan *et al.*, 1976
$\beta=[CuCl_2]/[Cu^{2+}][Cl^-]^2$	4.7 M^{-2}	30.1 M^{-2}	Khan *et al.*, 1976
$\beta=[CuCl_3^-]/[Cu^{2+}][Cl^-]^3$	2.0 M^{-3}	2.0 M^{-3}	Khan *et al.*, 1976
$\beta=[CuCl_4^{2-}]/[Cu^{2+}][Cl^-]^4$	0.23 M^{-4}	0.23 M^{-4}	Khan *et al.*, 1976

Table 3 shows the calculated equilibrium concentrations of copper- and gold species in standard leaching conditions. Thermodynamic instability of uncomplexed cuprous, aurous and auric ions are illustrated as their concentrations are very low, whereas uncomplexed cupric ions accumulate rather mediocre concentrations. In comparison, chloride complexes accumulate rather high concentrations. (McDonald *et al.*, 1987)

Table 3. Equilibrium concentrations of gold and copper species. Initial conditions are T = 102 °C, $[CuCl_2]$ = 0.6 M, $[NaCl]$ = 3.42 M, $[HCl]$ = 0.1 M. (Modified after McDonald *et al.*, 1987)

Complex species	Concentration (mol/l)
Au^{3+}	1.33×10^{-31}
$AuCl_4^-$	6.01×10^{-5}
Au^+	6.68×10^{-15}
$AuCl_2^-$	5.50×10^{-4}
Cu^{2+}	1.19×10^{-3}
$CuCl^-$	0.064
$CuCl_2$	0.402
$CuCl_3^-$	0.095
$CuCl_4^{2-}$	0.037
Cu^+	1.4×10^{-17}
$CuCl_2^-$	1.4×10^{-17}
$CuCl_3^{2-}$	1.4×10^{-17}

5.2 Bromide

Gold dissolution rate, in bromide system, is very fast at neutral pH conditions (Aylmore, 2005). This can be predicted by the electrode potential of the oxidation reaction (Equation 23). Dissolution rates are several orders of magnitude faster than that of cyanide leaching. Bromide leaching is effective for sulfide minerals and refractory materials, because they do not require separate pre-treatment. (Marsden & House, 2006) However, bromide complexes are more instable than cyanide, yet more stable than chloride complexes as presented in Table 1.

$$Au + 2Br^- + Br_2 \Leftrightarrow AuBr_4^- + e^- \qquad E^0 = 0.95\ (V) \qquad (23)$$

Bromide complexation with gold is similar to that of chloride. Au^{3+} is more stable than Au^+ in aqueous solutions when $pH < 3$ and temperature below 50 °C. Increasing temperature increases $AuBr_2^-$ concentration, but increasing bromide and proton activities favors $AuBr_4^-$. $AuBr_4^-$ complex is square planar by geometry and it has tendency to transform into linear $AuBr_2^-$ with increase in entropy, while system is heating. This transformation is demonstrated in Equation 24. (Pan, 1993)

$$AuBr_4^- + H_2O \Leftrightarrow AuBr_2^- + 2Br^- + 2H^+ + ½O_2 \qquad (24)$$

Bromide is noted to be accelerating gold dissolution from iron and sulfur containing ores in cupric chloride and alkali chloride containing media. Only little amounts of bromide, 0.5–30 g/l (0.006–0.38 M), are required in order to enhance chloride system. (Haavanlammi *et al.*, 2010) Abe & Hosaka (2010) argue that suitable bromide ion concentration ranges from 1 to 50 g/l (from 0.013 to 0.63 M) and the optimally from 10 to 25 g/l (from 0.13 to 0.31 M). Bromine additions in chloride leaching processes increase oxidative power and stability of gold chloride complexes (Ahtiainen & Lundström, 2016). Bromide ions also form complexes with metals that have higher concentration than gold, such as copper and iron. However, hardly any bromides are consumed due to the complexation as redundant iron and copper are recovered from the solution, leaving bromide ions in the solution for further use. (Abe & Hosaka, 2010)

5.3 Iodide

Gold iodide complex is the most stable halide gold complex in aqueous solution. This is due to the lower redox potential value compared to chloride and bromide. Gold dissolution rate in iodide system proportionally rises with increase in iodide concentration and pH has minimal effect in range of 2-10. (Aylmore, 2005) Hiskey *et al.* (1988) argued

that AuI_2^- complex is stable in pH range of 0-13 at potential range 500-700 mV vs. SHE (corresponding 256-456 mV vs. SCE). Iodide-system is a possible method for leaching sulfide minerals. However, iodide is very expensive, therefore, recovery and regeneration of the active species is crucial from the economic point of view. (Aylmore, 2005) According to Baghalha (2012), only very low amount of iodine is required for Au extraction, since gold extraction of 89% was reached with solution containing 20 g/l iodide and 4 g/l iodine.

It is typical for iodine to react with iodide to form I_3^- with Au^+ instead of forming the Au^{3+} complex in aqueous iodine system. Au^{3+} oxidizes iodide ion to iodine, thus, Au^{3+} is instable and reduced to Au^+-complex. Equation 25 illustrates the overall Au^+-iodide complex formation. (Aylmore, 2005) Total reaction for Au^{3+} iodide complex formation is presented in Equation 26 (Wang *et al.*, 2013).

$$2\,Au + I_3^- + I^- \Leftrightarrow 2AuI_2^- \quad (25)$$

$$2\,Au + 3I_3^- \Leftrightarrow 2AuI_4^- + I^- \quad (26)$$

Solubility of solid iodine in pure water is very low and the dissolution reaction is presented in Equation 27. However, presence of iodide ions causes solid iodine to dissolve and to form tri-iodide ions in solution with pH less than 9, as presented in Equation 28. While pH is higher than 9, hypoiodite and iodate are also formed in the solution. These are shown in Equations 29 and 30. (Baghalha, 2012)

$$I_2(s) \Leftrightarrow I_2(aq) \quad (27)$$

$$I_2(s) + I^- \Leftrightarrow I_3^- \quad (28)$$

$$I_3^- + H_2O \Leftrightarrow IO^- + 2I^- + 2H^+ \quad (29)$$

$$3I_3^- + 3H_2O \Leftrightarrow IO_3^- + 8I^- + 6H^+ \quad (30)$$

6 Industrial processes

6.1 Batch leaching

Batch leaching experiments are a suitable method for studying practicality of leaching solution and its functionality with the raw material. Batch leaching is uncommon for commercial purposes, thus mainly used in research purposes. However, only little amount of cupric chloride batch leaching experiments are published. Table 4 shows examples from patents, with cupric and ferric ions as oxidizing agents as well as chloride and bromide ions as complexing agents. Abe & Hosaka (2010, 2013) applied low amounts of oxidants, cupric ions ranging from 2 to 15 g/l (0.03–0.2 M) and ferric ions from 0.7 to 2 g/l (0.01–0.04 M). Secondly, 60 g/l (0.94 M) cupric ions were used by Haavanlammi *et al.* (2010). However, chloride concentration is more coherent varying from 81 to 183 g/l (2.3–5.2 M). Raw materials were sulfidic copper concentrates, whose copper and iron contents were utilized as oxidants.

Table 4. Compilation of batch leaching experiments in literature, from which dissolution rates were calculated.

Time (h)	pH	T (°C)	Oxidant (g/l)	Complexing agent (g/l)	Gold grade (ppm)	Dissolution rate (mg/h)	Extraction (%)	Reference
15	0.5-2.5	90	$[Cu^{2+}]$ = 60	$[Cl^-]$ = 152 $[Br^-]$ = 12	7	1.6	90.0	Haavanlammi *et al.*, 2010
16	1.5-2.0	85	$[Cu^{2+}]$ = 12 $[Fe^{3+}]$ = 0.7	$[Cl^-]$ = 180 $[Br^-]$ = 17	66	0.214	4.11	Abe *et al.*, 2010
2.7	1.3-1.7	85	$[Cu^{2+}]$ = 15	$[Cl^-]$ = 186 $[Br^-]$ = 20	82	10.3	47.60	Abe *et al.*, 2010
80	1-1.4	85	$[Cu^{2+}]$ = 2.4 $[Fe^{3+}]$ = 1.8	$[Cl^-]$ = 81	73	0.236	50.7	Abe *et al.*, 2010
4	0.8-1	85	$[Fe^{3+}]$ = 2	$[Cl^-]$ = 183 $[Br^-]$ = 19	20	0.876	40.0	Abe *et al.*, 2010
80	0.9-1.2	85	$[Cu^{2+}]$ = 2 $[Fe^{3+}]$ = 1.7	$[Cl^-]$ = 118 $[Br^-]$ = 19	73	0.341	72.6	Abe *et al.*, 2010
24	0.5-1.9	85	$[Cu^{2+}]$ = 12 $[Fe^{3+}]$ = 1.7	$[Cl^-]$ = 180 $[Br^-]$ = 17	43	0.394	82.2	Abe *et al.*, 2013

6.2 Continuous leaching

Continuous leaching is typical in industry. Currently there is no commercialized gold chloride leaching plants in operation, although, there has been patented systems and pilot plants. Majority include cupric and/or ferric ions as oxidants, with bromide ions improving dissolution rate. Additionally, chloride leaching introduces the possibility of exploiting oxidative elements in the raw material. (Aylmore, 2016) Abe & Hosaka (2010) mention in their patent that iron and copper contained in the raw material can be leached and used for leaching gold, thus reducing reagent costs.

Abe & Hosaka (2013) investigated the effect of replacing the leaching solution as a function of time. Leaching solution consisted of 25 g/l cupric, 5 g/l ferric, 180 g/l chloride and 22 g/l (0.39, 0.09, 5.1, 0.28 M, respectively) bromide ions. Air sparge was conducted in the reactors to regenerate the oxidants. Gold grade in raw material was 43 ppm and leaching lasted 24 hours, where in the first experiment the solution was not replaced and in the second experiment, the solution was replaced every three hours. As a result, gold grade in leach residue was 28 ppm with no solution replacement, whereas gold grade lowered to 10 ppm, when solution was replaced. Therefore Abe & Hosaka (2013) argued that the gold concentration in the solution during gold leaching affects the gold leaching rate.

Intec Gold Process is a gold processing method by an Australian technology company, which focuses on minerals processing. In the leaching process, gold concentrate is fed to reactors, where sulfides are oxidized with direct air and oxygen injection. Leaching media contains chloride or bromide concentration of 6–8 M and cupric concentration of 20–60 g/l (0.31–0.94 M) at temperature 85–95 °C. Customarily the residence time is 3–4 hours, but it can be up to 10 if the leaching kinetics and mineral composition of the concentrate requires it. (Intec Ltd., 2009)

Similar process is HydroCopper^{TM} by Outokumpu, in which copper concentrate is leached in sodium chloride solution with copper chloride. Temperature varies in the range of 85–95 °C and pH 1.5–2.5. Iron is oxidized by blowing air or oxygen into the leaching reactor and precipitated as hydroxide or oxide. When most of the sulfide minerals are dissolved, redox potential is increased to dissolve gold. Gold can then be recovered with chemical precipitation or activated carbon. (Hyvärinen & Hämäläinen, 2005)

II EXPERIMENTAL PART

In the experimental part of this thesis, the effect of circumferential speed, cupric ion concentration, particle size, leaching duration, temperature and chloride ion concentration were investigated to find optimal conditions for gold extraction. Measurements were performed in laboratory of Hydrometallurgy and Corrosion in Aalto University, Finland. The purpose was to evaluate the effect of parameters on gold dissolution rate and extraction, in order to find the optimal leaching conditions within the investigated ranges. The measurements were carried out as batch leaching experiments, in titanium reactor with two different raw materials. These raw materials are described as raw material 1 and raw material 2, further in the thesis.

7 Experimental materials and methods

Two different gold containing low-grade raw materials, with composition similar to the tailings, were investigated. Particle size distributions of the raw materials were analyzed with Malvern Mastersizer 3000. Measurements were carried out with water and ultrasound dispersions. Two different raw materials were used and the first raw material comprised of two batches. Particle size distribution results are presented in Figure 13 and Figure 14, showing the distribution of un-sieved material used in majority of experiments with raw material 1 and 2. Red line depicts volume density percentage of corresponding particle size and green line depicts cumulative volume percentage. Median particle size was used to distinct particle sizes to coarse and fine, displaying the effect noticeably. Border with the raw material 1 was 75 µm and 45 µm with raw material 2.

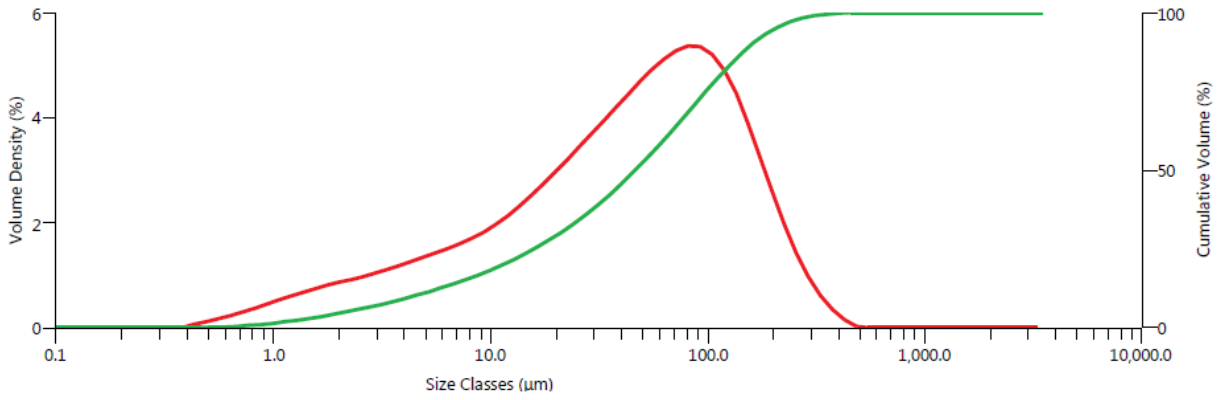


Figure 13. Particle size distribution of raw material 1. Red line describes volume density and green line cumulative volume of size classes.

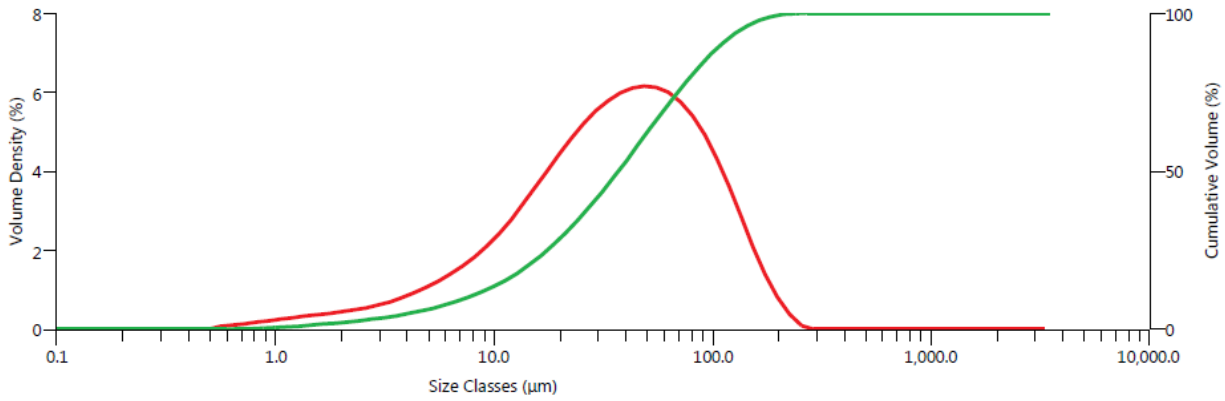


Figure 14. Particle size distribution of raw material 2. Red line describes volume density and green line cumulative volume of size classes.

The chemical compositions of both raw materials before any treatment (un-sieved) are presented in Table 5. This data is provided by Outotec. Both raw material 1 and 2 consisted mainly of silicon dioxide, with small amounts of other elements. However, it should be noted that raw material 1 contained 4.9% iron and raw material 2 contained 7.49% aluminum. Also gold content was higher in raw material 2 (4.93 ppm) than in raw material 1 (1.89 ppm). According to mineralogy analyses by Outotec, raw material 1 consisted primarily of quartz and feldspar (albite and anorthite), while the rest consisted mainly of actinolite and biotite, but also ilmenite. Main sulfide minerals are pyrite as pyrrhotite and chalcopyrite. Other minerals are arsenopyrite and löllingite, galena, apatite, barite, graphite, calcite and goethite. Raw material 2 composed mainly of quartz, while aluminum silicates (andalusite and kaolinite), micas and feldspars comprise almost the rest of the sample. Other important minerals are apatite, rutile, barite, monatzite and zircon. Main sulfide mineral is pyrite as pyrrhotite and chalcopyrite. Main tellurides include tellurobismuthite, altaite, frohbergite, hessite, rucklidgeite and coloradoite. Gold occurs mainly as fine-grained native grains with silver, but also in tellurides.

Table 5. Chemical composition of raw material 1 and 2 provided by Outotec.

Element/ compound	Material 1 Un-sieved	Material 2 Un-sieved	Unit
SiO_2	64.5	78.1	%
Te	-	<0.005	%
Ti	-	0.44	%
Mn	-	0.006	%
Na	-	0.16	%
K	-	1.43	%
Mg	-	0.33	%
Cr	-	0.008	%
Ca	-	0.3	%
Al	-	7.49	%
Cu	0.002	0.13	%
Fe	4.9	0.99	%
C	0.048	<0.05	%
Cl	0.024	<0.02	%
Ni	0.003	<0.005	%
Co	0.016	<0.005	%
Zn	0.014	<0.005	%
Pb	0.008	<0.02	%
S	0.21	0.35	%
Au	2.00	5.28	ppm
Ag	1.1	2.74	ppm
As	0.02	<0.005	%
Sb	0.01	<0.005	%
Bi	<0.005	<0.01	%
Hg	<0.002	-	%
Nb	0.00	-	%
Mo	<0.002	<0.005	%
Sn	0.00	-	%
W	<0.002	-	%
Ga	<0.003	-	%
Cl	0.04	<0.02	%
Th	0.00	-	%
U	<0.0005	-	%
Cs	0.00	-	%
La	0.00	-	%
Ce	0.01	-	%
Ta	<0.001	-	%

Both raw materials were sieved at median particle size to achieve coarse and fine fractions. Coarse fraction, in raw material 1, comprised of particles above 75 μm and fine

comprised of particles below 75 µm. Dividing particle size, with raw material 2, was 45 µm. While investigating other parameters than particle size, un-sieved material was used. To ensure the homogeneity of un-sieved raw material, raw material was first divided roughly with riffle splitter shown in Figure 15. Afterwards, a segment was divided with rotating sample divider to separate material into eight similar portions. This is shown in Figure 16.

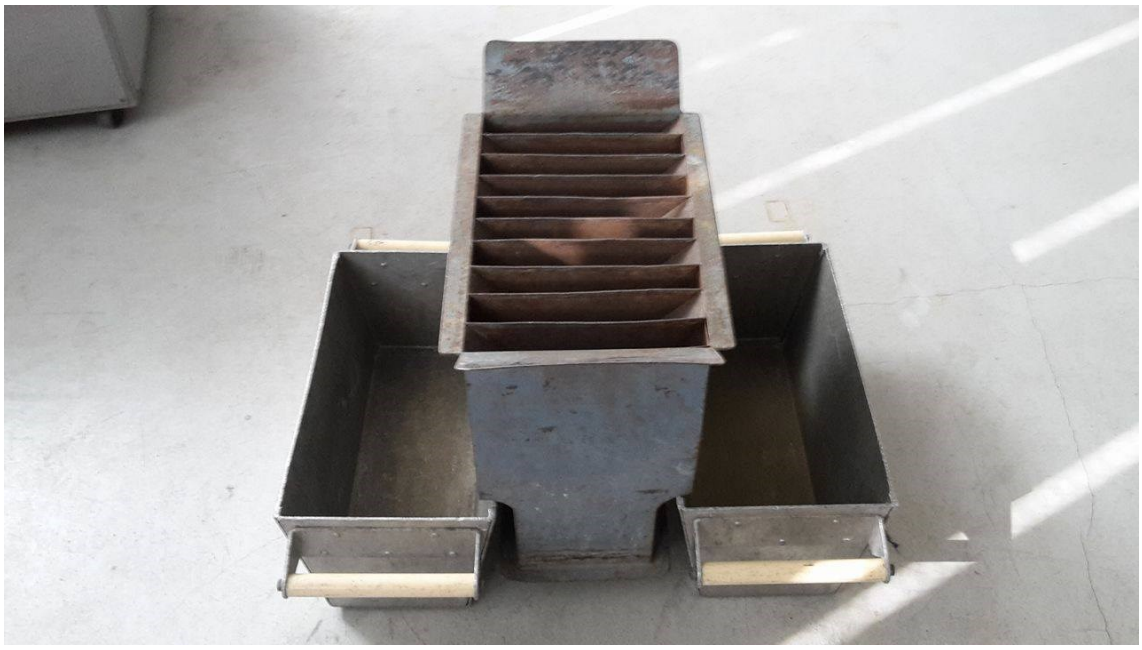


Figure 15. Riffle splitter used for dividing in half.

Figure 16. Rotating sample divider.

Leaching experiments were performed in a 3L OKTOP convex bottom titanium reactor with flow prevention baffles. The rotation of the system was performed with a VWR Vos

16 overhead stirrer equipped with a four-blade titanium impeller (45°) with diameter of 6.2 cm. The setup is presented in Figure 17. The oxygen sparge (Industrial grade, 99.5%) is directed to the bottom of the reactor via titanium pipe and it was adjusted with a rotameter to 1 l/min in every experiment. Additionally, reactor was equipped with thermometer, heating plate and condensing tube. Tested leaching solution contained cupric ions originating from technical grade copper chloride dehydrate (VWR Chemicals $CuCl_2 \cdot 2\ H_2O$). Additional chloride was achieved by adding technical grade sodium chloride (VWR Chemicals NaCl). NaCl is eligible due to high solubility of $NaAuCl_4$ compared to other salts (Senanayake, 2004). Adjustments to pH was performed by adding Eur. Grade hydrochloric acid (Merck KGaA, 32-37%). HCl was used, because it does not interfere with the process chemistry (Abe & Hosaka, 2010).

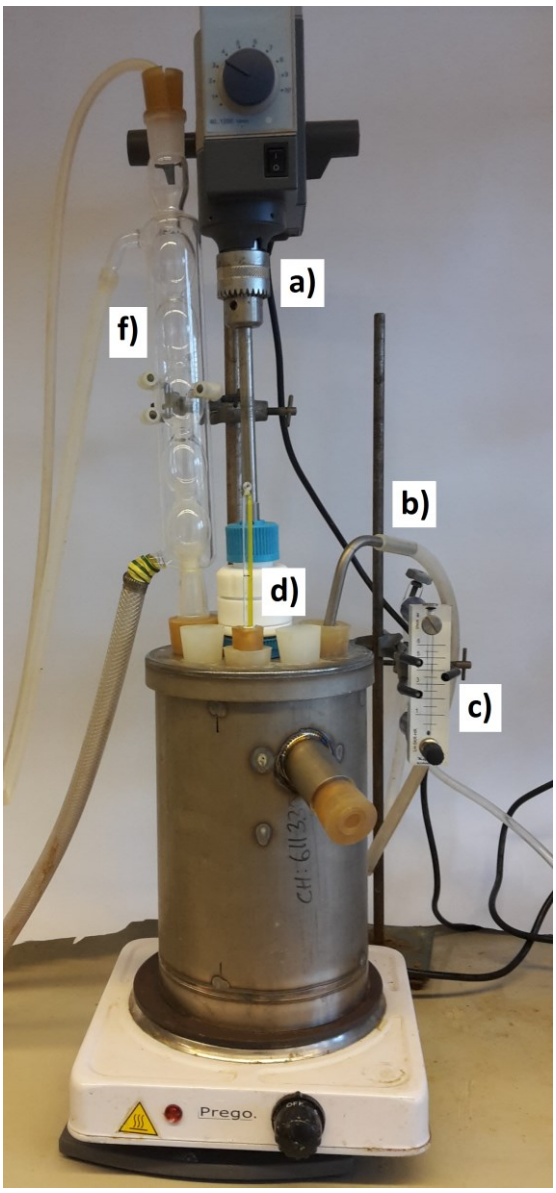


Figure 17. Testing setup for batch leaching equipped with a) overhead stirrer, b) oxygen sparge, c) rotameter, d) thermometer, e) heating plate and f) condensing tube.

The investigated conditions for leaching experiments, with raw material 1, are described in Table 6. It should be noted that experiments 1.1, 1.7 and 1.12, as well as 1.4 and 1.14 had the same conditions and they were performed to clarify the reproducibility of tests. Conditions used in experiments 1.1, 1.7 and 1.12 were considered the standard conditions and they remain constant in every experiment, save for single varying parameter. Rotational speed of 310 RPM was used in experiments corresponding the circumferential speed of 1 m/s. Additionally 500 RPM, corresponding to the circumferential speed of 1.6 m/s, was tested. Circumferential speed of 1 m/s was chosen for being the minimum value causing suspension in the reactor. Cupric ion concentration varied between 0.2−1.0 M as well as chloride concentration between 1−5 M. These concentration ranges were noted to be optimal according to literature (McDonald, 1987; von Bonsdorff *et al.*, 2005; Lampinen *et al.*, 2017; Abe & Hosaka, 2010). During the experiment, 1 l/min oxygen was continuously fed in the reactor to regenerate reduced cuprous ions back to cupric ions. The pH of solution was set to 1 and kept below 2.0, though the desired pH was between 1-1.5, during the experiment by adding 37% HCl. HCl was added constantly with a pipette and recorded. The insertion rate was higher in the beginning of the experiment, since pH increased more rapidly. Leaching time was four hours, but also two and six hours experiments were carried out in order to achieve kinetic data based on solid residue analyses. Small sample of solids was taken after one hour during the two hour leaching experiment (Experiment 11). Solids content was fixed to be 20% in all experiments, with 2.35 l solution volume and 2.5 l total volume. Combination of extremum parameters was also tested in experiment 1.15. Raw material in experiments 1.1–1.10 were from a different batch as in experiments 1.11–1.19, however the difference between both batches in particle size and precious metal content was within error margin.

Table 6. Investigated parameters in leaching experiments with raw material 1.

Experiment number	Leaching time (h)	Circumferential speed (m/s)	Particle size	$[Cu^{2+}]$ (M)	$[Cl^-]$ (M)	Temperature (°C)
1.1	4	1	Un-sieved	0.5	3	95
1.2	4	1.6	Un-sieved	0.5	3	95
1.3	4	1	Un-sieved	1	3	95
1.4	4	1	Un-sieved	0.2	3	95
1.5	4	1	Coarse	0.5	3	95
1.6	4	1	Fine	0.5	3	95
1.7	4	1	Un-sieved	0.5	3	95
1.8	4	1	Un-sieved	0.5	3	75
1.9	4	1	Un-sieved	0.5	5	95
1.10	4	1	Un-sieved	0.5	1	95
1.11	2	1	Un-sieved	0.5	3	95
1.12	4	1	Un-sieved	0.5	3	95
1.13	6	1	Un-sieved	0.5	3	95
1.14	4	1	Un-sieved	0.2	3	95
1.15	4	1.6	Un-sieved	1.0	5	95
1.16	4	1	Un-sieved	0.5	3	85
1.17	4	1	Un-sieved	0.5	3	65
1.18	4	1	Un-sieved	0.5	4	95
1.19	4	1	Un-sieved	0.5	2	95

To investigate reaction kinetics, solution samples were taken as well as redox potential and pH was measured at times 0, 10, 30, 60, 90, 120, 150, 180, 210, 240, 270, 300, 330 and 360 min. The volume of sample was 10 ml, however it included small fraction of residue. Therefore, the samples were filtered and thereafter preserved with 5 drops of 2 M nitric acid, dosed with a plastic pipette. Due to sampling and evaporation, 30 ml cupric chloride solution was added into system at 60, 120 and 180 min in order to keep the solution volume as constant as possible. The additive volumes were defined beforehand with evaporation test. Redox was measured with Orbisint CPS12 electrode by Endress+Hauser against Ag/AgCl in two-electrode system. pH was measured with Orbipac CPF81 electrode by Endress+Hauser.

The experiment conditions and parameters with raw material 2, are depicted in Table 7. The experimental setup was similar to the setup of experiments 1.1–1.10 with material 1, although there were several changes. Standard conditions were the same, apart from circumferential speed, which was increased to 1.1 m/s (340 RPM) to achieve suspension with raw material 2. In addition, the effect of circumferential speed was investigated by increasing it to 1.7 m/s (530 RPM). Cupric chloride concentration remained the same as

with raw material 1, except experiment 2.4, where cupric concentration was 0.1 M instead of 0.2 M. This was performed to further signify the effect of cupric ion concentration. Intermediate values of 0.3 M and 0.75 M were also investigated. Similarly, the effect of temperature was investigated by increasing the temperature intervals from 10 to 15 °C, resulting in investigating temperatures 50 and 80 °C. Chloride concentration was retained the same. Leaching time was investigated only by increasing it to 6 h. Unlike with raw material 1, pH was kept below 2 instead of 1.5 during experiments. Initial pH was 1, however, pH was adjusted with 33% HCl. Although solids content was also 20%, only 2.1 l solution was required for total volume of 2.5 l.

Table 7. Parameters in leaching experiments with raw material 2

Experiment number	Leaching time (h)	Circumferential speed (m/s)	Particle size	$[Cu^{2+}]$ (M)	$[Cl^-]$ (M)	Temperature (°C)
2.1	4	1.1	Un-sieved	0.5	3	95
2.2	4	1.7	Un-sieved	0.5	3	95
2.3	4	1.1	Un-sieved	1	3	95
2.4	4	1.1	Un-sieved	0.1	3	95
2.5	4	1.1	Coarse	0.5	3	95
2.6	4	1.1	Fine	0.5	3	95
2.7	4	1.1	Un-sieved	0.5	3	95
2.8	4	1.1	Un-sieved	0.5	3	65
2.9	4	1.1	Un-sieved	0.5	5	95
2.10	4	1.1	Un-sieved	0.5	1	95
2.11	4	1.1	Un-sieved	0.5	3	95
2.12	6	1.1	Un-sieved	0.5	3	95
2.13	4	1.1	Un-sieved	0.3	3	95
2.14	4	1.1	Un-sieved	0.75	3	95
2.15	4	1.1	Un-sieved	0.5	2	95
2.16	4	1.1	Un-sieved	0.5	4	95
2.17	4	1.1	Un-sieved	0.5	3	50
2.18	4	1.1	Un-sieved	0.5	3	65
2.19	4	1.1	Un-sieved	0.5	3	80

After the experiment, residue was washed with distilled water, which was removed by filtering and decanting. This was performed until the residue was clean. Afterwards, the moist residue was dried in oven.

Fire-assay was used for solids analysis and they were performed by Labtium oy. Fire-assay is a traditional gold analysis method for gold concentrations between 0.1 and 50 ppm. It is prevalent due to its accuracy, consistency and economic efficiency. In this method, samples are mixed with litharge (PbO) and glass-forming fluxes. Samples should be grounded finely so that 80–90% of material has particle size <75 µm. Flux charge is

placed in a crucible and heated in a muffle furnace at 850 °C. Temperature is further raised to 1000 °C over a period of 30–40 minutes or until complete fusion has occurred. In the process, lead circulates through the molten charge, collecting precious metals and forming gold-silver-lead alloy. Alloy is separated from the glass slag, containing base metals and other impurities, and the lead is removed by cupellation. The cupel is preheated at 1000 °C for lead removal. Remaining metal pill is either weighed, parted by dissolving silver in nitric acid and reweighed for gold content or dissolved entirely in aqua regia. This solution is further analyzed for gold and silver by AAS or ICP techniques. (Marsden & House, 2006) Solution analysis was performed with inductively coupled plasma mass spectrometry (Thermo Scientific iCAP Q ICP-MS) by Outotec Oy.

The results of fire assay analysis of raw materials are presented in Table 8. Raw material 1 contains below 2 ppm gold in all fractions. Therefore, sieving raw material had only little effect on gold concentration. However, raw material 2 contained 4.93 ppm gold and sieving the material resulted in significant differences in gold concentration. Fine fraction contained 8.66 ppm, while un-sieved and coarse fractions contained 4.93 and 2.92 ppm, respectively. Silver concentration was similarly more dominant in smaller particles. It should be noted that there is a major difference in silver concentration in un-sieved raw material 2 compared to the chemical composition characterization provided by Outotec (1.6 vs. 2.74 ppm). Nonetheless, fire-assay result (Table 8) was used to define both gold and silver extractions further in the thesis.

Table 8. Gold and silver concentrations in raw materials.

		Au (ppm)	Ag (ppm)
Raw Material 1	Un-sieved	1.89	1.1
	Fine	1.98	
	Coarse	1.61	
Raw Material 2	Un-sieved	4.93	1.6
	Fine	8.66	2.6
	Coarse	2.92	0.9

The extractions from solids samples are calculated using Equation 31, where dry residue mass ($m_{residue}$) (Presented in Appendix F) multiplied with gold content in residue (c_{solids}) is subtracted from initial gold mass (m_0). This is divided with initial gold mass. The extractions from solution samples are calculated with Equation 32, where gold concentration ($c_{solution}$) is multiplied with the solution volume (V) in the reactor during the moment of sampling. The sum of previous samples concentrations (Σc_{sample}) of the

experiment are multiplied with sample volume (V_{sample}), added to the previous term and divided with initial gold mass (m_0). The volume is estimated from evaporation, additions and samples with the final solution volume (Appendix G). Dissolution rate is calculated with Equation 33, where m_0 is initial gold mass, $m_{residue}$ is the mass of dry residue, c_{solids} is the gold content in residue, M_{Au} is the molar mass of gold and t is the time required for leaching all the gold. Time is achieved from solution analysis, by determining the point where solution extraction curve begins to flat to estimate when dissolution is mainly finished.

$$E_{solids} = \frac{(m_0 - m_{residue} * c_{solids})}{m_0} \quad (31)$$

$$E_{solution} = \frac{c_{solution} * V + \sum c_{sample} * V_{sample}}{m_0} \quad (32)$$

$$v = \frac{\frac{m_0 - m_{residue} * c_{solids}}{M_{Au}}}{t} \quad (33)$$

8 Results

8.1 Gold extraction in batch leaching experiments

Table 9 presents the gold and silver extractions based on solid and solution analyses with raw material 1. Experiments 1−10 comprise of the first batch and experiments 11−19 of the second. Solution analysis was performed for experiments 11−19 to define kinetics. However, they were noted to be more inaccurate, therefore, solid analyses were used to determine the extractions. Gold extractions varied between 66.2 and 88.2%, whilst silver extraction varied between 63 and 88.5%. The highest gold extraction was achieved in experiment 1.15, with extremum parameter values. Circumferential speed and chloride concentration had a clear positive effect on gold extraction. Cupric ion concentration, particle size and leaching duration affected gold extraction partly although no clear linear effect can be observed. Increase in temperature resulted in inconsistent results with solids analysis and in contradiction to literature, did not increase gold extraction. However, gold extractions were significantly lower if calculated based on solution analyses. Gold concentration in residue and solution samples are presented in Appendix A and B.

Table 9. Gold and silver extractions with raw material 1. Extractions were calculated based on solid and solution analyses in the end of retention time.

Experiment Number	Au extraction based on solid analysis (%)	Ag extraction based on solid analysis (%)	Au extraction based on solution analysis (%)	Ag extraction based on solution analysis (%)
1.1	71.5	-	-	-
1.2	77.4	-	-	-
1.3	77.1	-	-	-
1.4	72.3	-	-	-
1.5	68.8	-	-	-
1.6	71.7	-	-	-
1.7	72.2	-	-	-
1.8	67.3	-	-	-
1.9	82.1	-	-	-
1.10	66.2	-	-	-
1.11 (1h)	72.8	63	71.9	131.9
1.11	72.0	81.5	73.8	142.7
1.12	70.3	73.4	45.4	176.5
1.13	74.8	81.9	42.5	103.7
1.14	71.8	78.3	44.7	133.4
1.15	88.2	80.5	119.4	280.6
1.16	74.8	78.4	43.1	141.3
1.17	72.8	88.5	30.1	141.2
1.18	72.3	85.1	32.5	82.1
1.19	73.8	81.9	47.2	117.3

Table 10 shows gold dissolution rates with raw material 1. According to solution analysis, leaching was finished in approximately 2 h. Therefore, dissolution rate was calculated at 2 h. Distinctly highest dissolution rate was achieved at 1 h measuring point in experiment 1.11, however it is approximately two times higher than majority of other experiments. This indicates that dissolution reactions have finished before 1 h. This seems to be random error, as in this case solids sample was taken from the reactor during the experiment. The sample was significantly smaller than the residues in other experiments, causing inaccuracy in the analysis. Overall, variance in dissolution rate was low in experiments with raw material 1.

Table 10. Gold dissolution rates in leaching experiments with raw material 1.

Experiment Number	Dissolution Rate (mol/s)
1.1	$4.76 \cdot 10^{-10}$
1.2	$5.16 \cdot 10^{-10}$
1.3	$5.14 \cdot 10^{-10}$
1.4	$4.82 \cdot 10^{-10}$
1.5	$3.90 \cdot 10^{-10}$
1.6	$5.00 \cdot 10^{-10}$
1.7	$4.81 \cdot 10^{-10}$
1.8	$2.24 \cdot 10^{-10}$
1.9	$5.47 \cdot 10^{-10}$
1.10	$4.41 \cdot 10^{-10}$
1.11 (1h)	$9.71 \cdot 10^{-10}$
1.11	$4.80 \cdot 10^{-10}$
1.12	$4.69 \cdot 10^{-10}$
1.13	$4.99 \cdot 10^{-10}$
1.14	$4.79 \cdot 10^{-10}$
1.15	$5.88 \cdot 10^{-10}$
1.16	$4.98 \cdot 10^{-10}$
1.17	$2.43 \cdot 10^{-10}$
1.18	$4.92 \cdot 10^{-10}$
1.19	$4.82 \cdot 10^{-10}$

Gold and silver extractions for raw material 2 are shown in Table 11. Gold extractions ranged from 33.2% to 78.3% and silver extractions from 89.5% to 97.8%. Extractions based on solution analysis were significantly lower than those achieved with solids analysis, although solution analysis are more coherent with solids analysis with raw material 2 than raw material 1. This is most likely due to higher gold concentration in solution, allowing more accurate solution analysis. Nonetheless, solids analysis is used, while considering extractions, as they are more accurate than solution analysis with high copper and chloride concentrations and Au concentrations in the range of 0.02–0.6 ppm. Chloride ions, circumferential speed and particle size increased the gold extraction significantly. Temperature had inconsistent results, however the trend showed that increasing temperature also increases gold extraction. Cupric concentration increased gold extraction slightly, however, excessive amounts resulted in rapid decrease. Gold concentration in residue and solution samples are presented in Appendix A and B.

Table 11. Gold and silver extractions with raw material 2 leaching experiments based on solids and solution.

Experiment number	Au extraction based on solid analysis (%)	Ag extraction based on solid analysis (%)	Au extraction based on solution analysis (%)	Ag extraction based on solution analysis(%)
2.1	63.1	95.2	30.7	140.1
2.2	73.7	95.7	32.2	138.3
2.3	54.8	95.1	23.4	161.6
2.4	56.2	95.2	20.8	101.5
2.5	41.8	89.5	26.4	163.0
2.6	78.3	97.8	24.1	118.0
2.7	58.3	95.2	27.6	148.1
2.8	63.3	95.3	12.4	129.4
2.9	68.5	95.5	44.8	133.5
2.10	33.2	94.7	7.5	143.3
2.11	64.8	88.2	-	-
2.12	71.1	88.4	34.2	160.0
2.13	59.6	88.5	-	-
2.14	64.4	84.3	-	-
2.15	45.7	81.7	-	-
2.16	60.0	89.9	-	-
2.17	50.8	79.1	-	-
2.18	49.9	81.5	-	-
2.19	62.9	77.5	-	-

Variance in gold dissolution rate with raw material 2 was wider (Table 12). The highest dissolution rate was achieved with fine particle size, resulting in $1.20 \cdot 10^{-9}$ mol/s, while lowest dissolution rate was achieved with coarse particle size, which resulted in $2.15 \cdot 10^{-10}$ mol/s. In general, dissolution rates were higher and had more variance in experiments with raw material 2. This comparison excludes experiments with different leaching duration than 4 h (experiments 1.11 and 1.13).

Table 12. Gold dissolution rates in leaching experiments with raw material 2.

Experiment number	Dissolution rate (mol/s)
2.1	$5.48 \cdot 10^{-10}$
2.2	$6.40 \cdot 10^{-10}$
2.3	$4.76 \cdot 10^{-10}$
2.4	$4.88 \cdot 10^{-10}$
2.5	$2.15 \cdot 10^{-10}$
2.6	$1.20 \cdot 10^{-9}$
2.7	$5.07 \cdot 10^{-10}$
2.8	$5.50 \cdot 10^{-10}$
2.9	$5.95 \cdot 10^{-10}$
2.10	$2.89 \cdot 10^{-10}$
2.11	$5.63 \cdot 10^{-10}$
2.12	$4.94 \cdot 10^{-10}$
2.13	$5.18 \cdot 10^{-10}$
2.14	$5.60 \cdot 10^{-10}$
2.15	$3.97 \cdot 10^{-10}$
2.16	$5.21 \cdot 10^{-10}$
2.17	$4.41 \cdot 10^{-10}$
2.18	$4.34 \cdot 10^{-10}$
2.19	$5.47 \cdot 10^{-10}$

8.1.1 Effect of leaching duration

In experiments 1.11-1.13 with raw material 1, the effect of leaching duration was investigated. Figure 18 a shows only little difference in gold extraction between one and six hour of leaching time. Therefore, it can be concluded that vast majority of the free gold in the raw material was dissolved within the first hour of leaching, although, the possibility for random error exists. With raw material 2, leaching time had a distinct effect on gold extraction, as it increased from 58–65% to 71%, when leaching duration was increased from 4 to 6 has presented in Figure 18 b. Therefore, all possible gold could not be leached within 4 hours. Solution analyses showed that gold concentration in solution increased as function of time with raw material 2 presented in Figure 19. However, gold concentration has not evened out in experiments 2.1 and 2.7, further indicating the leaching reaction is not complete within 240 min. However, in experiment 2.12 gold extraction peak is achieved in 300 min, from which it decreased slightly, yet it indicates that the leaching was finished in 300 min.

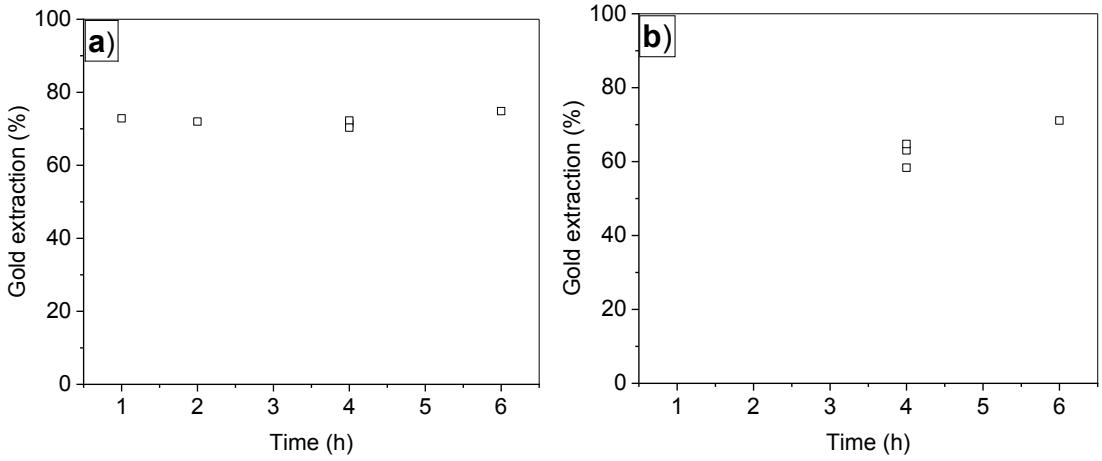


Figure 18. The effect of leaching duration on gold extraction with a) raw material 1 (Experiments 1.1, 1.7, 1.11, 1.12 and 1.13) and b) raw material 2 (Experiments 2.1, 2.7, 2.11 and 2.12). Parameters in the experiment were t = 1–6 h, $[Cu^{2+}]$ = 0.5 M, $[Cl^-]$ = 3 M, T = 95 °C, CS (Circumferential speed) = 1.1 m/s and raw material was un-sieved.

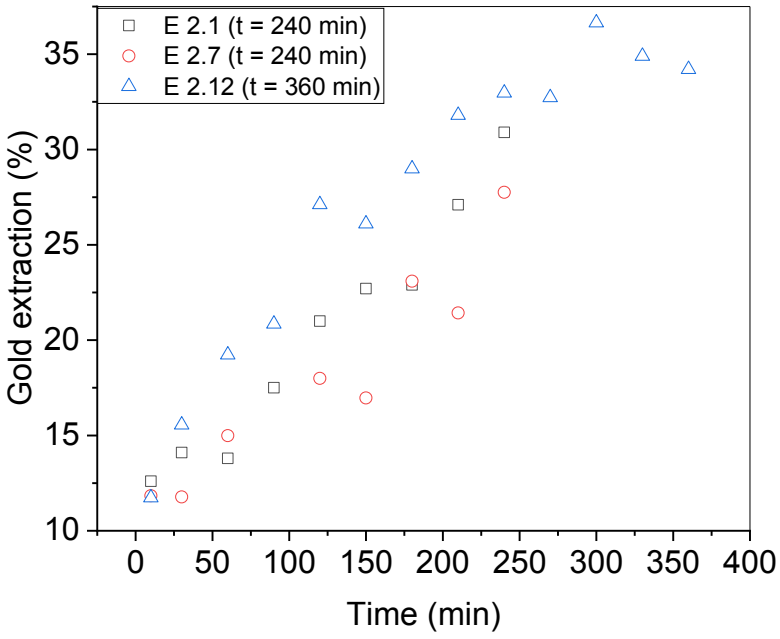


Figure 19. Gold extraction as function of time with raw material 2, according to solution analysis. Parameters in the experiment were t = 4–6 h, $[Cu^{2+}]$ = 0.5 M, $[Cl^-]$ = 3 M, T = 95 °C, CS = 1.1 m/s and raw material was un-sieved.

8.1.2 Effect of circumferential speed

In all measurements, suspension was reached and no raw material was stuck piled up on the reactor bottom. However, as seen in Figure 20 a and b, increase in circumferential speed increased gold extraction significantly: 6% units with raw material 1 and 13% units with raw material 2. The effect of circumferential speed is not clear though, as only two

different circumferential speeds were measured. Solution analysis presented in Figure 21 show that the leaching reactions did not finish within the experiment with raw material 2. Gold dissolved more rapidly, when circumferential speed was increased to 1.7 m/s compared to experiments with circumferential speed of 1.1 m/s.

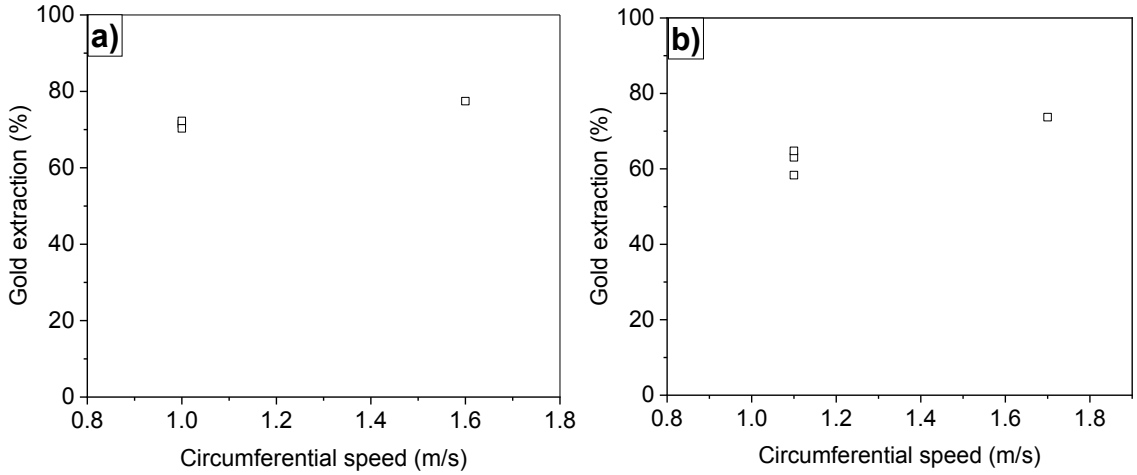


Figure 20. Gold extraction based on solid analyses as a function of circumferential speed with a) raw material 1 (Experiments 1.1, 1.2, 1.7 and 1.11) and b) raw material 2 (Experiments 2.1, 2.2, 2.7 and 2.11). Parameters in the experiment were t = 4 h, $[Cu^{2+}]$ = 0.5 M, $[Cl^-]$ = 3 M, T = 95 °C and raw material was un-sieved.

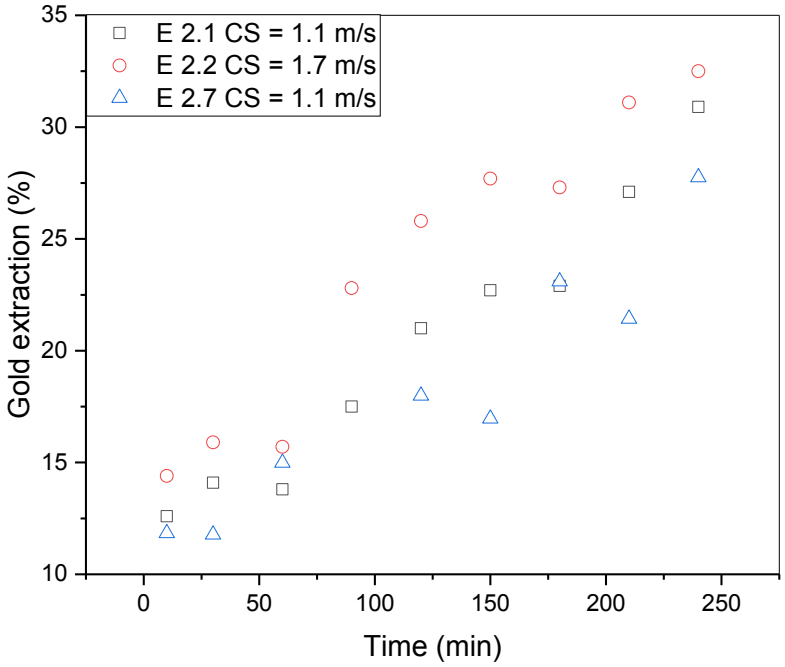


Figure 21. The effect of circumferential speed on gold extraction as a function of time in experiments with raw material 2, according to solution analysis. Parameters in the experiment were CS = 1.1–1.7 m/s, $[Cu^{2+}]$ = 0.5 M, $[Cl^-]$ = 3 M, T = 95 °C, t = 4 h and raw material was un-sieved.

8.1.3 Effect of particle size

Gold content in finer fraction was higher than in coarse fraction with both tested materials as presented in Figure 22 a and b. Particle size are marked in the figure as following: fine as 1, un-sieved as 2 and coarse as 3. With raw material 1, gold extraction rate with un-sieved and fine material were similar, whereas coarse material resulted in lower extraction. Although gold extraction of fine material achieved near identical results to un-sieved material, it should be noted that fine material was more abundant on gold, resulting in more gold in solution. However, gold extraction increased linearly with raw material 2 and the differences were more noticeable. Coarse fraction resulted in 41.8% extraction, un-sieved in average of 60.7% and fine in 78.4%. Leaching reactions did not finish within the 4 hour experiments according to extractions defined from solution analyses as presented in Figure 23.

Contrary to solids analysis, solution analysis presented in Figure 23 resulted in higher gold extraction with un-sieved material than fine material with raw material 2 up until 210 min. Sample taken at 240 min in experiment 2.6 with fine particle size was broken during transportation, resulting in no value. Since the gold concentration did not moderate as a function of time, leaching is not finished.

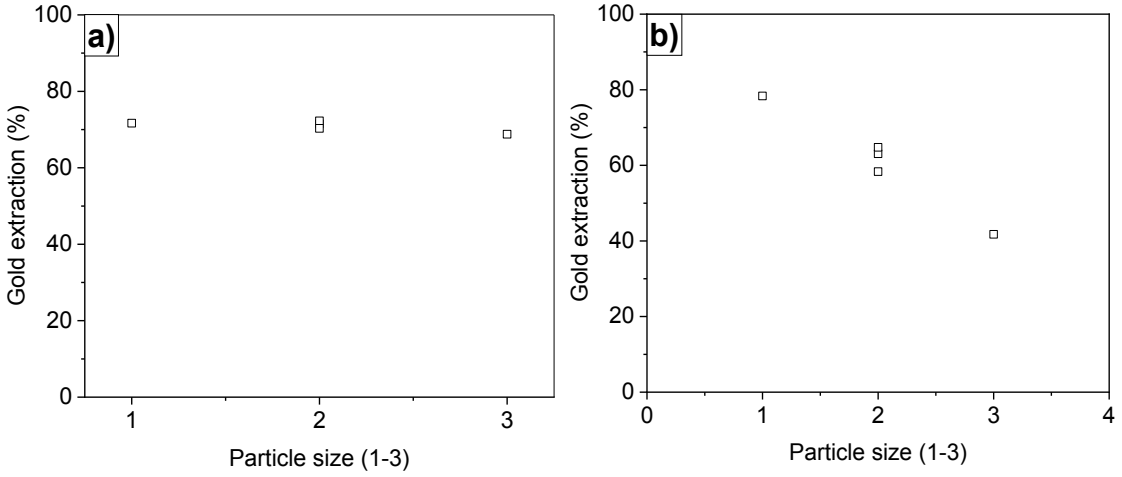


Figure 22. Gold extraction based on solid analyses as a function of particle size with a) raw material 1 (Experiments 1.1, 1.5, 1.6, 1.7 and 1.12) and b) raw material 2 (Experiments 2.1, 2.5, 2.6, 2.7 and 2.11). Particle size 1 corresponds fine fraction, 2 un-sieved and 3 coarse. Parameters in the experiment were t = 4 h, $[Cu^{2+}]$ = 0.5 M, $[Cl]$ = 3 M, T = 95 °C and CS = 1.1 m/s.

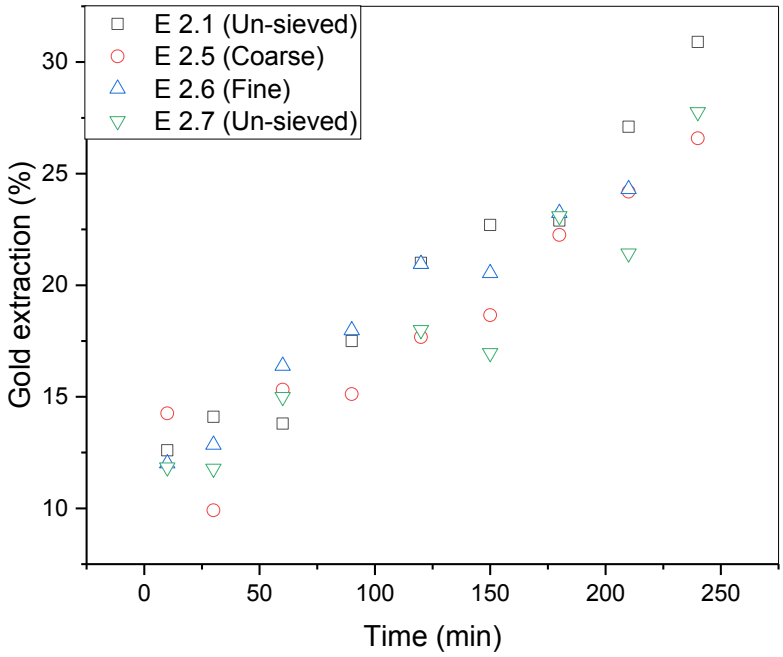


Figure 23. The effect of particle size on gold extraction as a function of time with raw material 2, according to solution analysis. Parameters in the experiment were $[Cu^{2+}]$ = 0.5 M, $[Cl^-]$ = 3 M, T = 95 °C, CS = 1.1 m/s and t = 4 h.

8.1.4 Effect of cupric ion concentration

Effect of cupric ion concentration was investigated with concentrations of 0.2, 0.5 and 1 M with raw material 1 and 0.1, 0.3, 0.5, 0.75 and 1 M with raw material 2. Figure 24 a shows no difference in extractions between 0.2 and 0.5 M. However, with material 2, gold extraction increased slightly up until 0.75 M, after which extraction rate fell rapidly. Cupric ion concentration of 1 M resulted in lowest results, whereas 0.75 M and one experiment with 0.5 M achieved best results as displayed in Figure 24 b. Figure 25 shows the gold extraction as function of time with varying cupric ion concentration. There is variation in the results between $[Cu^{2+}]$ = 0.1 and $[Cu^{2+}]$ = 1 M, however it is still indicated that $[Cu^{2+}]$ = 0.5 M is more favorable to them.

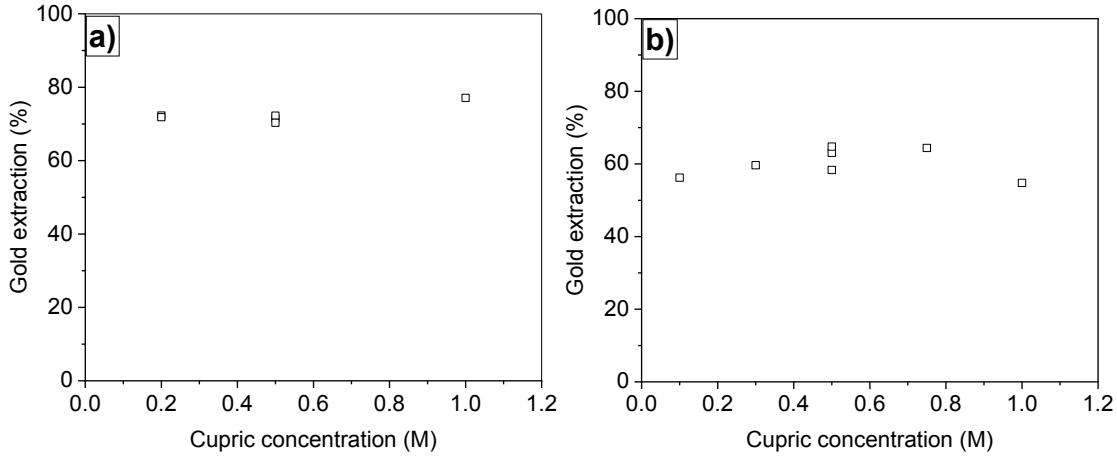


Figure 24. Gold extraction based on solid analyses as a function of cupric ion concentration with a) raw material 1 (Experiments 1.1, 1.3, 1.4, 1.7, 1.12 and 1.14) and b) raw material 2 (Experiments 2.1, 2.3, 2.4, 2.7, 2.11, 2.13 and 2.14). Parameters in the experiment were t = 4 h, $[Cl^-]$ = 3 M, T = 95 °C, CS = 1.1 m/s and raw material was un-sieved.

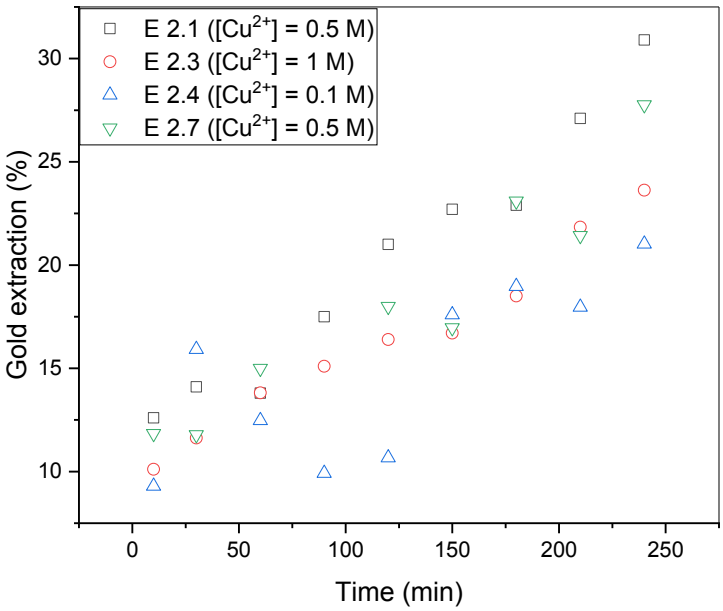


Figure 25. The effect of cupric concentration on gold extraction as a function of time with raw material 2, according to solution analysis. Parameters in the experiment were $[Cu^{2+}]$ = 0.1–1 M, $[Cl^-]$ = 3 M, T = 95 °C, CS = 1.1 m/s, t = 4 h and raw material was un-sieved.

8.1.5 Effect of chloride ion concentration

Chloride concentration was noted to have a clear impact on gold extraction. With raw material 1, chloride concentration was the most affecting factor, as the highest extraction rate (82.1%) was achieved with chloride concentration of 5 M, when the extremum experiment 1.15 was excluded. Further, chloride concentration of 1 M resulted in the lowest extraction (66.2%). Although, as Figure 26 a shows, gold extraction remained nearly the same when chloride concentration was between 2 and 4 M with raw material 1. However, increasing chloride concentration to 5 M, resulted in significant improvement in extraction, while chloride concentration of 1 M resulted in the lowest gold extraction. Similarly, Figure 26 b presents linear growth of gold extraction as a function of chloride concentration with raw material 2. Exception occurs, when chloride concentration is increased from 3 M to 4 M, with 4 M generally resulting in lower extraction than 3 M. Chloride concentration of 5 M resulted in highest gold extraction rate and 1 M in lowest. Figure 27 shows clear distinction between chloride concentration of 1 and 5 M, while also indicating low stability of gold chloride complexes, when $[Cl^-]$ = 1 M. Additionally, leaching reactions did not finish in four hours, thus higher extraction rates are possible.

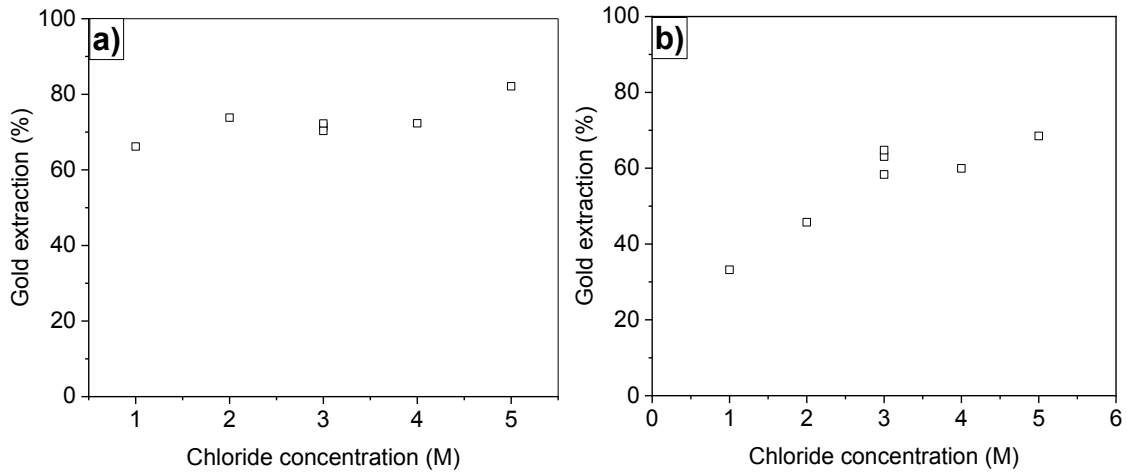


Figure 26. Gold extraction based on solid analyses as a function of chloride ion concentration with a) raw material 1 (Experiments 1.1, 1.7, 1.9, 1.10, 1.12, 1.18 and 1.19) and b) raw material 2 (Experiments 2.1, 2.7, 2.9, 2.10, 2.11, 2.15 and 2.16). Parameters in the experiment were t = 4 h, $[Cu^{2+}]$ = 0.5 M, T = 95 °C, CS = 1.1 m/s and raw material was un-sieved.

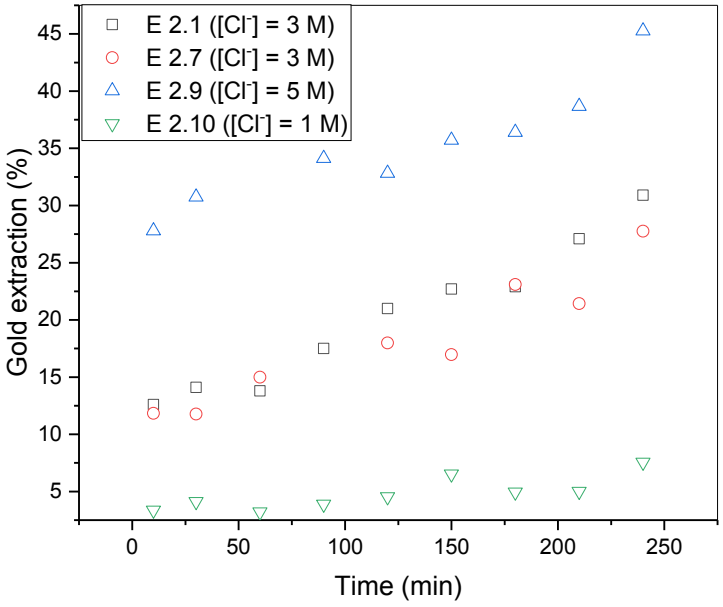


Figure 27. The effect of chloride concentration on gold extraction as a function of time with raw material 2, according to solution analysis. *[Cl⁻]* = 1–5 M, *[Cu²⁺]* = 0.5 M, *T* = 95 °C, CS = 1.1 m/s, *t* = 4 h and raw material was un-sieved.

8.1.6 Effect of temperature

Contrary to literature review, temperature did not show any distinct effect on gold extraction rate for neither raw materials in the investigated parameter range, according to extractions based on solid analyses. As demonstrated in Figure 28 a, leaching at 85 °C and 65 °C gave slightly higher final leaching extraction than at 95 °C and 75 °C with the first raw material. Additionally, extraction rate had no distinction between 95 and 80 °C for raw material 2, displayed in Figure 28 b. Gold extractions in experiments at temperature of 65 °C varied significantly, indicating a random error on either of them. Temperature of 50 °C resulted in unambiguously low gold extraction. However, gold concentration in solution was significantly lower in experiment 2.8 with T = 65 °C, than the others, as presented in Figure 29. Therefore, it could suggest a random error in solids analysis of experiment 2.8.

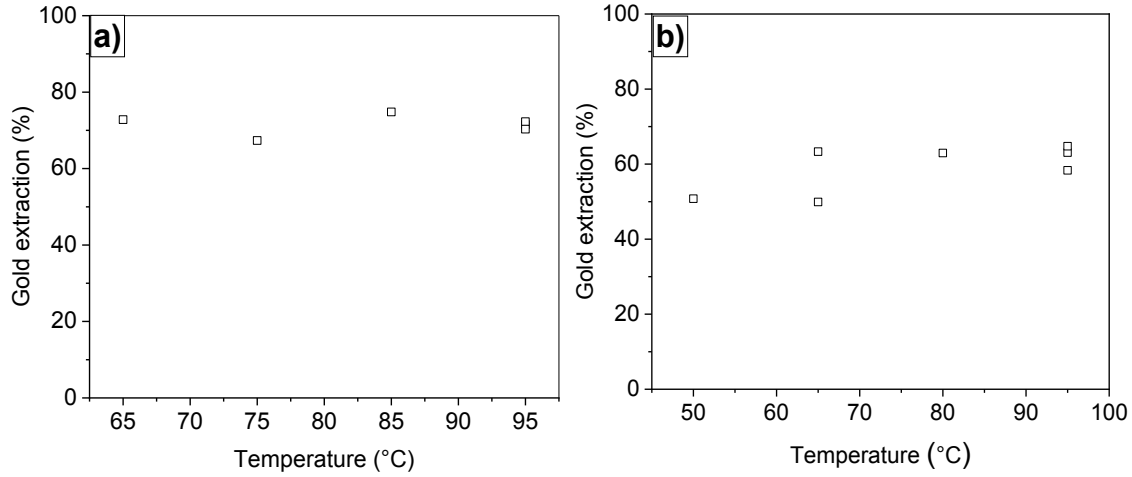


Figure 28. Gold extraction based on solid analyses as a function of temperature with a) raw material 1 (Experiments 1.1, 1.7, 1.8, 1.12, 1.16 and 1.17) and b) raw material 2 (Experiments 2.1, 2.7, 2.8, 2.11, 2.17, 2.18 and 2.19). Parameters in the experiment were *t* = 4 h, *[Cu^{2+}]* = 0.5 M, *[Cl⁻]* = 3 M, CS = 1.1 m/s and raw material was un-sieved.

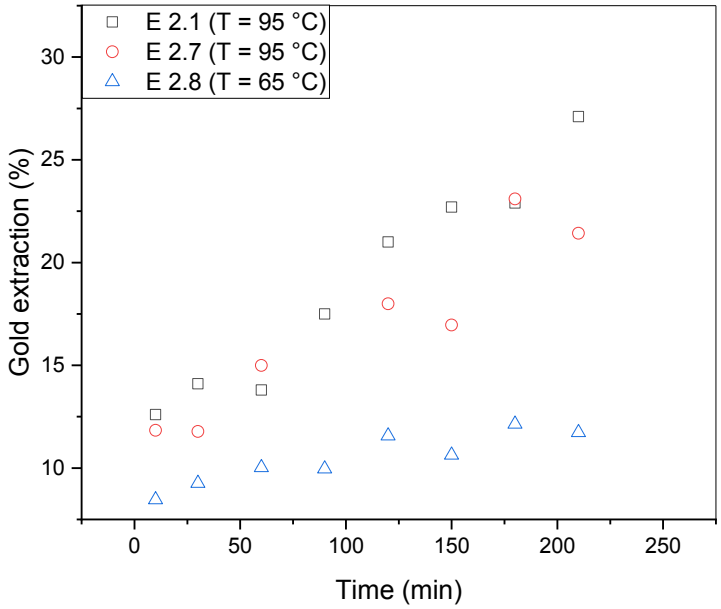


Figure 29. The effect of temperature on gold extraction as a function of time with raw material 2, according to solution analysis. *T* = 65–95 °C, *[Cl⁻]* = 3 M, *[Cu^{2+}]* = 0.5 M, CS = 1.1 m/s, *t* = 4 h and raw material was un-sieved.

8.2 Silver extraction in batch leaching

According to the results of leaching raw material 1, temperature is suggested to be the most affecting factor on silver extraction. This differs from the behavior of gold shown in Figure 28 a and b. The highest extraction rate of silver (88.5%) was achieved with the lowest temperature (T = 65 °C), while the lowest extraction (73.4%) leaching experiments was achieved with the highest temperature (T = 95 °C). Only leaching experiments, which lasted 4 h, are taken into comparison. Silver concentrations in samples are shown in Appendix C.

Silver concentration in residues of the first test series (experiments 2.1-2.10) of raw material 2 were below 0.2 ppm, excluding experiment 2.4, in which silver concentration was precisely 0.2 ppm. This indicates that silver concentration was below analysis limit, thus exact concentration nor extraction cannot be determined. However, almost all silver was dissolved, leaving only a tiny amount to show a response in the solid analyses. Near complete dissolution of silver is also supported by solution analysis presented in Table 11Table 12, where silver extraction rates exceed 100%. In experiments 2.11–2.19 small amounts of silver was found in every residue and silver extraction rates ranged between 77.5% and 89.5%. Because gold extraction in same experiments were coherent, it is possible for systematic error in the analysis phase of silver. Generally, more HCl was also added in experiments 2.11–2.19 than in 2.1–2.10, however, the difference is minimal compared to initial chloride concentration.

Silver extraction rates varied with the change in particle size of the second raw material. It should be noted that this is caused by difference in silver grade of raw material. Silver grade in fine fraction was 2.6 ppm and 0.9 ppm in coarse fraction. This initial concentration alters the extraction rates and shows as wider difference, when the silver concentration in both leach residues is the same, even though near zero.

8.3 Redox potential in batch leaching

Redox potential was recorded vs. Ag/AgCl and then converted to potential vs. SCE. Figure 30 a-f and Figure 31 a-f represent redox potential as a function of time in experiments with raw materials 1 and 2, respectively. It can be observed that the redox potential of the leaching solution declined rapidly from approximately 650 to 350–500 mV vs. SCE after the insertion of raw material to the leaching reactor. This illustrates consumption of initial oxidative species. Thereafter, redox potential begun to rise as the applied oxygen sparge oxidized cuprous ions and other dissolved metallic species in the solution. However, there was no clear pattern for redox increase. Figure 30 a and Figure 31 a show that increased circumferential speed cause the redox potential to rise more steeply after the initial drop. As displayed in Figure 30 b, with raw material 1, fine particle size resulted in lower redox potential after the material was fed, but there was no difference between coarse and un-sieved material. During the experiment, redox potential rose on the same level with un-sieved material and nearly same level as with coarse material. As seen in Figure 31 b, fine and un-sieved particle sizes resulted in equal redox potential after feeding the material. On the other hand, coarse particle size resulted in higher redox potential after feeding the material. Figure 30 c and Figure 31 c present that higher cupric concentration result in higher redox potential, as expected by Nernst equation. Figure 30 d and Figure 31 d show that chloride concentration had no consistent effect on redox potential. According to Figure 30 e and Figure 31 e, lower temperature results in lower redox potential, however, the trend is inconsistent. Figure 30 f shows remarkable variation in redox potentials until 240 min, even though the leaching conditions were the same in every experiment. After 240 min, redox increases slowly. With raw material 2, redox potentials were more identical as presented in Figure 31 f and after 240 min, redox potential rises slowly.

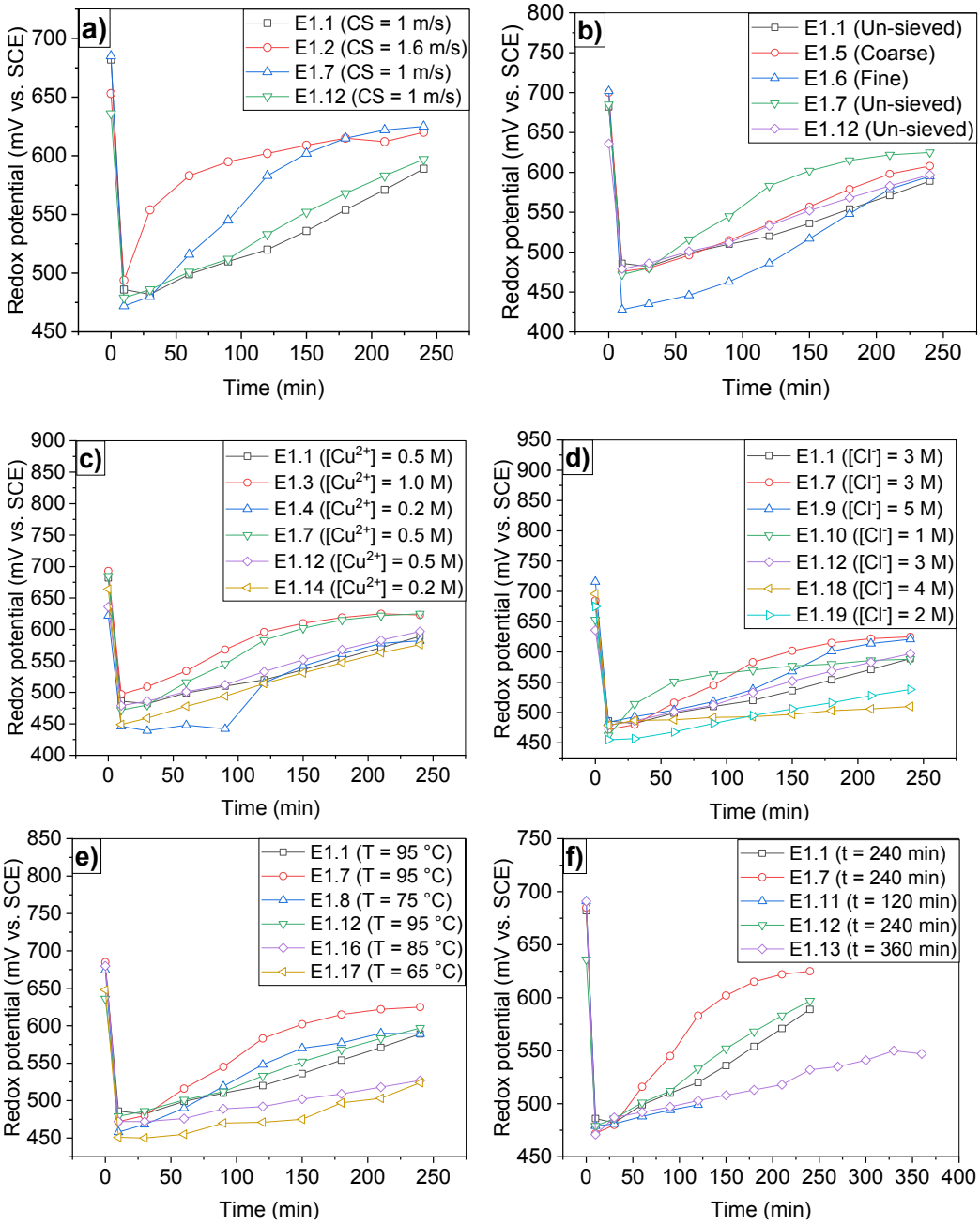


Figure 30. Redox potential as a function of a) circumferential speed, b) particle size, c) cupric concentration, d) chloride concentration, e) temperature and f) time with raw material 1. Constant parameters in the experiment were t = 4 h, $[Cu^{2+}]$ = 0.5 M, $[Cl^-]$ = 3 M, CS = 1 m/s, T = 95 °C and raw material was un-sieved, while one parameter was changed at the range shown in the figure.

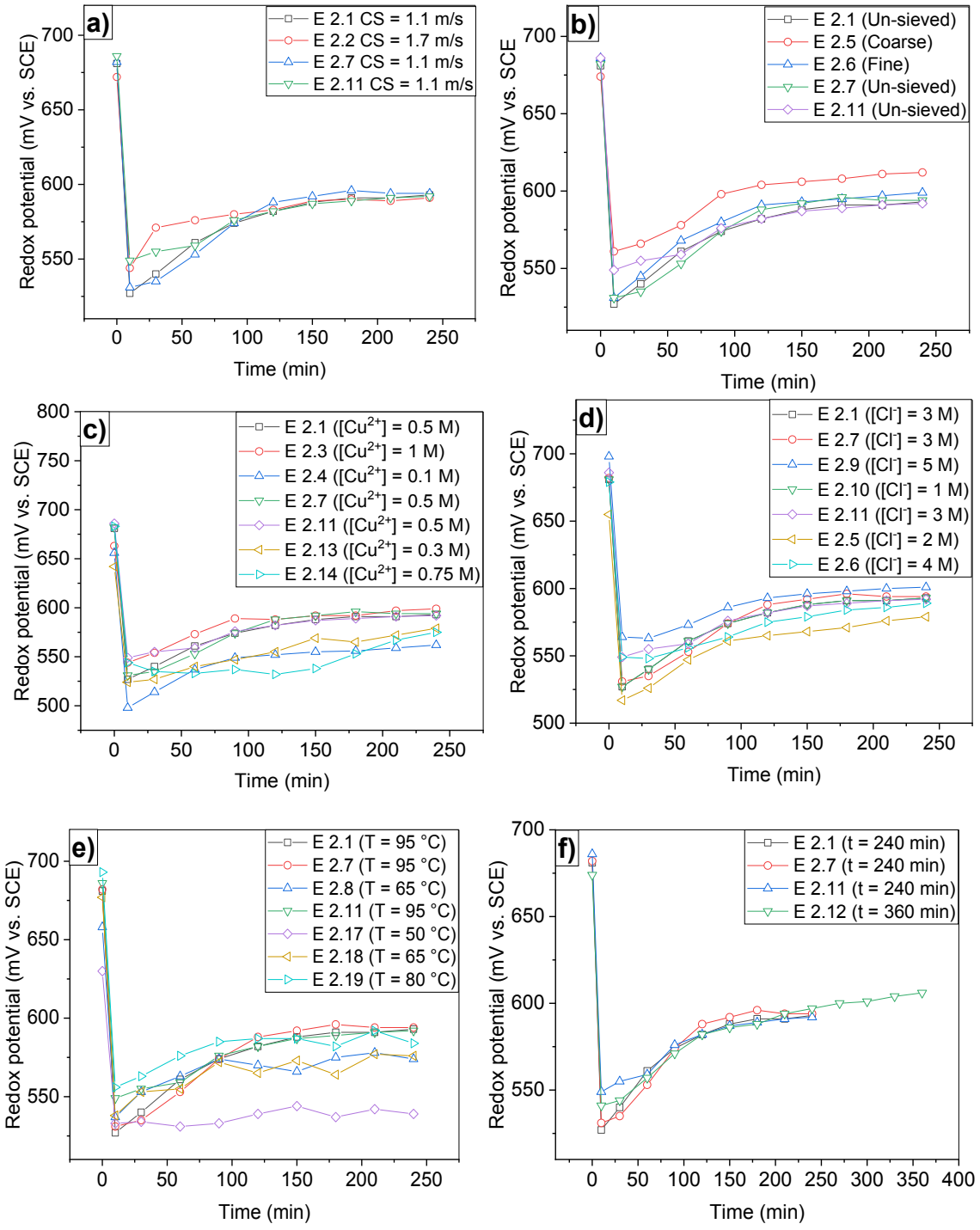


Figure 31. Redox potential as a function of a) circumferential speed, b) particle size, c) cupric concentration, d) chloride concentration, e) temperature and f) duration with raw material 2. Constant parameters in the experiment were t = 4 h, $[Cu^{2+}]$ = 0.5 M, $[Cl^-]$ = 3 M, CS = 1 m/s, T = 95 °C and raw material was un-sieved, while one parameter was changed at the range shown in the figure.

8.4 pH in batch leaching

In the measurements, the effect of pH was kept reasonably constant and its effect was not investigated. pH variation depends primarily on the amount of added HCl and HCl additions as function of time are presented in Appendix D. Solution pH was adjusted to 1 in all experiments, although it was kept below 1.5 with raw material 1 and below 2 with raw material 2. This was performed with 37% and 32% HCl, respectively. HCl additions with raw material 1 were significantly higher than with raw material 2, since desirable pH was between 1.0 and 1.5 instead of 1.5 and 2.0. Another reason is the high iron content in raw material 1 presented in Table 5. As demonstrated in Figure 32 and Figure 33, pH exceeded 2 rapidly after the raw material was fed. HCl additions were thus required to regenerate cuprous ions to cupric ions as the reaction consumes hydrogen ions (Equation 11). Still, the most important component in regeneration is oxygen. As mentioned earlier, cuprous ions are formed oxidizing gold, when cupric ions are reduced (Equations 5 and 6).

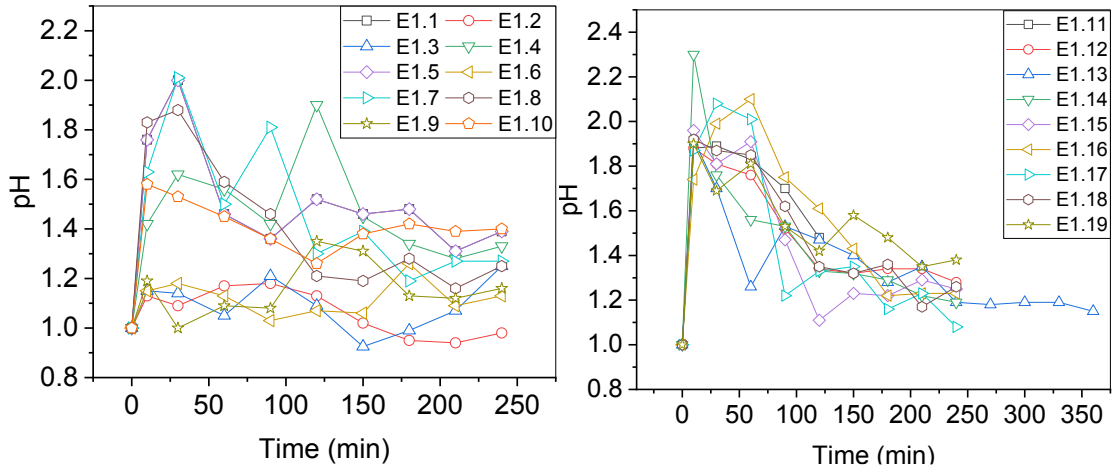


Figure 32. pH during leaching experiments with raw material 1.

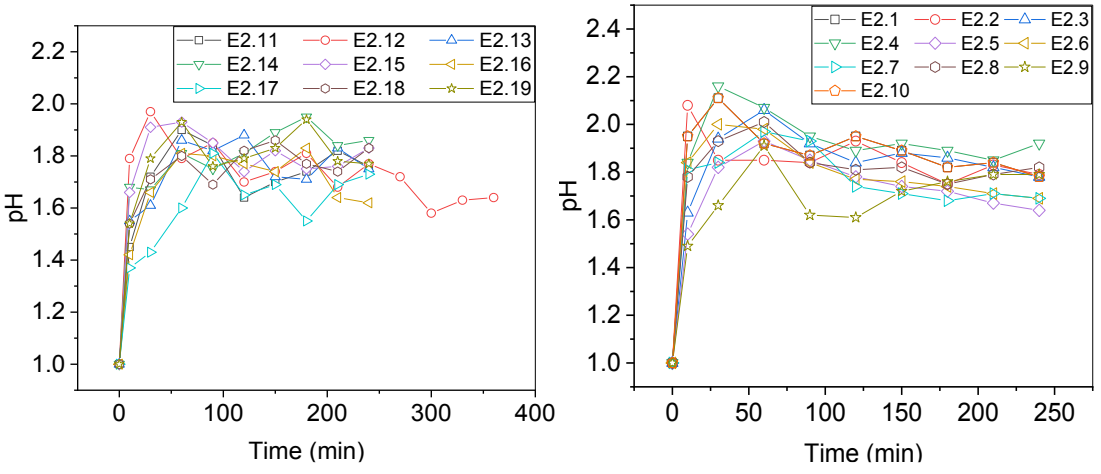


Figure 33. pH during leaching experiments with raw material 2.

Table 13 shows the HCl additions and standardized acid consumption required for kilogram of raw material during the leaching experiments. With raw material 1, pH was kept below 1.5, while with raw material 2 below 2, which explains the different magnitude of additions. As seen in Table 5, raw material 1 contains more iron, which could also affect high acid consumption. In principal, more HCl was required in experiments with higher gold extraction rate, lesser cupric ion concentration and higher temperature. Furthermore, with raw material 2 especially, particle size made a notable difference.

Table 13. HCl additions and acid consumption per kilogram of raw material during the leaching experiments. 37% HCl was used in experiments with raw material 1 and 33% HCl with raw material 2.

Raw material 1	HCl additions (ml)	Acid consumption (g/kg)	Raw material 2	HCl additions (ml)	Acid consumption (g/kg)
1.1	94	223	2.1	12	27.9
1.2	60	142	2.2	12	27.9
1.3	55	130	2.3	8	28.6
1.4	104	246	2.4	11	25.6
1.5	88	208	2.5	8	18.6
1.6	95	225	2.6	15	34.9
1.7	65	265	2.7	14	32.6
1.8	83	197	2.8	12	27.9
1.9	79	187	2.9	5	11.6
1.10	63	149	2.10	13	30.3
1.11	65	154	2.11	4	9.3
1.12	105	249	2.12	6	14.0
1.13	80	189	2.13	5	11.6
1.14	111	263	2.14	6	14.0
1.15	80	189	2.15	8	18.6
1.16	80	189	2.16	4	9.3
1.17	80	189	2.17	1	2.3
1.18	100	237	2.18	2	4.7
1.19	70	166	2.19	3	7.0

9 Discussion

In this thesis, gold leaching in cupric chloride media was investigated by literature review and laboratory measurements. The purpose of laboratory measurements was to examine the effect of various parameters on gold extraction and dissolution rate in batch leaching experiments. These parameters included leaching duration, circumferential speed, particle size, cupric concentration, chloride concentration and temperature and they were investigated with two different raw materials. Additionally, silver extraction was investigated. In this chapter, these parameters affecting gold dissolution rate and extraction are discussed.

9.1 Raw material

Current gold ores and increasingly more difficult to process and require arduous pretreating before cyanidation process. Chloride based leaching opens up possibilities in various complicated ore types. These consist mainly of sulfide ores with reductive nature. Additionally, tailings, which are left over cyanidation or flotation processes, could be reprocessed in chloride leaching process. Raw materials in laboratory experiments were tailings, which consisted mainly of SiO_2. Gold and silver content were both very low (1.89 and 1.11 ppm in raw material 1 and 4.93 and 1.6 ppm in raw material 2).

Experiments with raw material 1 resulted in less variance between gold extraction and dissolution rate, than experiments with raw material 2. Main differences in the raw material are high iron content in raw material 1 (4.9% vs. 0.99%), as well as higher gold and aluminum content and smaller particle size in raw material 2. Higher gold content and smaller particle size increase the reactive area, thus, causing the difference between favorable and unfavorable conditions more distinct. Additionally, metals with lower reduction potential than gold, such as aluminum, can reduce gold complexes to metallic gold. Relatively instable gold chloride complex is particularly prone for this. (Marsden & House, 2006) Therefore, gold reduction in gentler conditions, such as low chloride concentration, could explain significantly lower dissolution rate with raw material 2. Iron content in raw material 1 exceeded that of raw material 2 by 5 times. If all of iron dissolves in the solution, it results in approximately 0.22 M concentration, while, with raw material 2, it results in 0.045 M. However, either there was no difference with dissolved iron between raw material 1 and 2 or the results contradict with the results of Abe *et al.* (2013), as dissolution rates were near identical. Another explanation is that the dissolved iron is

not in the oxidizing ferric ion form as different oxidation number and formation of iron-chloride complexes decreases the oxidative power (Seisko *et al.*, 2018), however this is unlikely due to the strong oxygen sparge. Nevertheless, as mentioned before, the slight differences in dissolution rates can be caused by various reasons.

9.2 Leaching duration

The kinetics of cupric chloride leaching was investigated with solution analysis with both raw materials. Additionally, 1, 2, 4 and 6 h experiments were conducted on raw material 1, as well as 4 h and 6 h experiments on raw material 2, to gain more reliable kinetics based on solid analyses. In most of the experiments with raw material 1, majority of soluble gold was dissolved by 2 h, according to solution analysis and no significant variance was seen between 1, 2, 4 and 6 h in solids analysis. Contrarily, with raw material 2, leaching was still incomplete after 4 hours according to solution analyses, while solution analysis from 6 h experiment indicated that the leaching was finished in 5 h. Furthermore, extractions based on solid analyses between 4 and 6 h showed 6.3% unit difference.

9.3 Circumferential speed

Lampinen *et al.* (2017) claimed that circumferential speed increases mass transfer within the reactor. Agitation causes diffusion layer to thin, causing faster mass transfer of reacting species to the particle. This increases gold dissolution rate. As mass transfer increases, gold dissolution is even more controlled by charge transfer. Results of the conducted experiments support the effect of circumferential speed, as gold extraction increased, when circumferential speed was increased from 1 to 1.6 m/s (from 71.5% to 77.4%) and 1.1 to 1.7 m/s (from 63.1% to 73.7%) in experiments 1.2 and 2.2. Additionally, redox potential increased more rapidly after the initial drop in experiments 1.2 and 2.2 with high circumferential speed. This indicates that the diffusion layers of gold particles has thinned and also that oxygen sparge is mixed more thoroughly in the solution to regenerate cuprous ions to cupric ions and even ferrous ions to ferric ions, increasing the gold dissolution rate.

9.4 Particle size

As particle size is decreased, reactive area increases. Additionally, according to fire-assay/FAAS analysis, gold grade was higher in smaller particles with both raw materials. Because the gold is more prevalent in smaller particles, there is more likely less gangue material required to penetrate, for the lixiviant to reach the gold. Fine fraction resulted in higher gold extraction than coarse with both raw materials. No significant dissimilarity was noted with fine (71.7%) and un-sieved fraction (70.3–72.2%) with raw material 1, however, with raw material 2 fine fraction (78.3%) showed remarkable increase compared to both un-sieved (58.3 – 64.8%) and coarse (41.8%).

Fine particle size with raw material 1 resulted in lower redox potential up until 180 min than those of un-sieved and coarse fractions, as the reactive area is higher and more oxidizing species are spent initially. Redox potentials between experiments with un-sieved and coarse particle size contained only slight variance, with the exception of experiment 1.7, where redox increased more rapidly after 60 min. This did not occur with experiments 1.1 and 1.2, indicating it was a random error. Respectively, coarse particle size with raw material 2 resulted in higher redox potentials throughout the entire experiment. Lower redox potential among experiments with finer particle size implies more reactivity and consumption of reagents.

9.5 Cupric ion concentration

McDonald (1987) and Lampinen *et al.* (2017) suggested that cupric concentration enhances gold dissolution up until 0.6 M and then it levels or even diminishes. According to the experiments with raw material 1, however, there was no negative effect in increasing cupric concentration to 1 M. Vice versa, cupric concentration of 1 M resulted in the highest gold extraction rate of 77.1%. Cupric concentration of 0.2 and 0.5 M resulted in similar extractions, 72.3 and 71.8% when $[Cu^{2+}]$ = 0.2 M and 71.5, 72.2 and 70.3%, when $[Cu^{2+}]$ = 0.5 M. On the other hand, cupric concentration of 1 M resulted in the lowest gold extraction with raw material 2, when investigating the effect of cupric concentration. This supports the results presented in literature.

Several processes exploit the copper content of raw material as an oxidant, thus, reducing reagent costs. If left uncontrolled, this could detriment gold dissolution as the cupric concentration can rise to unsatisfactory amounts. Copper concentration in raw materials differed, although, copper concentration in raw material 2 (0.13%) was several

magnitudes higher than in raw material 1 (0.002%), it has only little effect on total cupric concentration in the solution even when fully dissolved. Fully dissolved copper amounts increased molarity of solution by 0.01 and $1.6 \cdot 10^{-4}$ M, respectively. Hence, the raw material copper concentration is not considered being the reason for differences in gold dissolution rate, when cupric concentration was 1 M.

9.6 Chloride ion concentration

In earlier studies, increasing chloride concentration is noted to increase gold dissolution rate (McDonald *et al.* 1987; von Bonsdorff, 2006 and 2007). In this thesis, chloride concentration of 1–5 M were examined. Based on the results chloride concentration had significant effect on gold dissolution. Chloride concentration of 1 M resulted in the lowest gold dissolution with both raw materials (66.2% and 33.2%), while 5 M resulted in second highest with raw material 1 (82.1%) and third highest with raw material 2 (68.5%). Regardless, no linear increment was noted between chloride concentration of 2–4 M.

9.7 Temperature

Temperature was suggested to be the most impactful parameter in cupric chloride gold leaching according to literature (McDonald *et al.*, 1987; von Bonsdorff, 2006; Lampinen *et al.*, 2017). However, temperature had ambiguous effect on gold extraction within investigated parameter range (50–95 °C). Instead, gold extraction rates remained equal, while temperature was decreased from 95 to 65 °C. On contrary to solid analysis, solution analysis showed lowest gold extraction (30.1% with raw material 1 and 12.4% with raw material 2) when T = 65 °C on both raw materials.

Redox potentials in experiments with altering temperature varied by temperature mainly, but also by gold extraction. In experiments with raw material 1, experiments 1.16 (T = 85 °C) and 1.17 (T = 65 °C) had final redox potential of approximately 70 mV lower than in experiments with standard conditions, with 527 and 524 mV vs. Ag/AgCl respectively (482 and 479 mV vs. SCE), compared to 600 mV vs. Ag/AgCl (555 mV vs. SCE) (presented in Appendix E). Still, these experiments resulted in slightly higher extraction rates (74.8% and 72.8%). Similarly, with raw material 2, redox potential in experiment 2.8 (T = 65 °C) was 20 mV lower than in experiments 2.1 and 2.7 (T = 95 °C). However, the differential in extraction was small and according to previous research, temperature

has significant impact on gold dissolution. Significant difference in redox potential occurred in experiment 2.17 (T = 50 °C), where redox potential remained between 533 and 544 vs. Ag/AgCl throughout the experiment. This clarifies the low gold extraction rate (50.8%). Heating plate caused issues at low temperatures, as the analog heat control could not be adjusted to 65 and 50 °C. Therefore, the temperature varied slightly in experiments with low temperature. Varation range was -5–5 °C of the wanted temperature. Additionally, heat was conducted only to the bottom of the reactor, causing uneven temperature within the reactor.

Solution analyses were generally more inaccurate than solid analyses. Still, they both followed similar trend with the exception of experiments, where the effect of temperature was investigated. In experiments with raw material 1, gold concentration in solution was lowest, when T = 65 °C, whereas, it was only slightly lower, when T = 85 °C, than when T = 95 °C. Similar trend occurred with raw material 2, where gold extraction was 12.5% when T = 65 °C and 31.0%, when T = 95 °C. Silver concentrations in these experiments were comparable with other experiments. Because this happened systematically, it is unlikely to be random error.

9.8 Combination of favorable parameters

Combination of favorable parameters (Circumferential speed = 1.6 m/s, $[Cu^{2+}]$ = 1 M, $[Cl^{-}]$ = 5 M) were used in experiment 1.15, resulting in highest gold extraction. Solution analyses illustrated that the gold extraction was continuing to rise after the experiment, resulting in higher extractability. This did not occur on other experiments with raw material 1, except for experiment 1.17 (T = 65 °C). Therefore, this combination of favorable parameters is possible to liberate locked gold, the leaching conditions in other experiments could not.

10 Conclusions

Interest in alternative leaching methods for current cyanide leaching processes is increasing due to safety and environmental issues. The aim of thesis was to determine the effect of different parameters on gold extraction and dissolution rate in cupric chloride media in a batch scale. Gold leaching was investigated with two raw materials. Raw material 1 was investigated with leaching duration of 1–6 h, cupric concentration of 0.2–1 M, circumferential speed of 1 and 1.6 m/s, chloride concentration of 1–5 M, temperature of 65–95 °C and particle size fractions of <75 µm, >75 µm and un-sieved fractions. Raw material 2 was investigated with leaching duration of 4 and 6 h, cupric concentration of 0.1–1 M, circumferential speed of 1.1 and 1.7 m/s, chloride concentration of 1–5 M, temperature of 50–95 °C and particle size fractions of <45 µm, >45 µm and un-sieved fractions. In every experiment standard parameters were t = 4 h, $[Cu^{+}]$ = 0.5 M, $[Cl^{-}]$ = 3 M, T = 95 °C, un-sieved particle fraction and circumferential speed was 1 m/s with raw material 1 and 1.1 m/s with raw material 2. Single parameters were altered to investigate its effect, apart from experiment where combination of favorable parameters were investigated.

The highest gold extraction with raw material 1 was achieved with combination of favorable parameters from previous experiments, resulting in 88.2% extraction. The conditions were t = 4 h, $[Cu^{+}]$ = 1 M, $[Cl^{-}]$ = 5 M, T = 95 °C, un-sieved particle fraction and circumferential speed was 1.6 m/s. 82.1% was achieved when $[Cl^{-}]$ = 5 M, 77.4% with circumferential speed of 1.6 m/s and 77.1% when $[Cu^{2+}]$ = 1 M. Lowest gold extraction rates were achieved when $[Cl^{-}]$ = 1 M and coarse particle size fraction of raw material, resulting in 67.3 and 68.8%, respectively. Rest of the gold extraction results varied between 70.3 and 74.8%, illustrating only slight variance within error margin. Contrary to literature, temperature was noted to have no effect on gold extraction, however, silver extraction rates were noted to increase with lowering the temperature. Overall, silver extractions were inconsistent and would require more research.

Raw material 2 contained more gold than raw material 1 and resulted in higher variance between gold extractions. The most impactful parameter was particle size, as fine particle size fraction resulted in gold extraction of 78.3%. Other important factors were increasing circumferential speed to 1.7 m/s and chloride concentration to $[Cl^{-}]$ = 5 M, resulting in 73.7 and 68.5%, respectively. Lowest extractions were resulted from $[Cl^{-}]$ = 1 M and coarse particle size fraction, resulting in 33.2 and 41.8%, respectively. Extraction rates in

other experiments were in range between 54.8 and 63.3%. Unlike with raw material 1, cupric concentration did not linearly increase gold extraction and the order of optimal cupric concentration was 0.75 M ≈ 0.5 M > 0.1 M > 1 M. Temperature was noted to have mixed effect on raw material 2. Increasing temperature from 80 °C to 95 °C had no impact on gold dissolution, however, lowering temperature to 65 °C gave mixed results, while lowering to 50 °C resulted in lower gold extraction. Altogether, temperature had impact on gold dissolution, although it was minor compared to previous studies. Furthermore, silver dissolved near entirely in every experiment.

In conclusion, chloride concentration, particle size fraction of raw material and circumferential speed were the most impactful factors for leaching gold in cupric chloride media with both raw materials. Cupric ion concentration requires accurate adjustments, depending on the raw material, while the effect of temperature is slightly unclear. Nevertheless, cupric chloride media offers a potential solution for leaching gold from certain raw materials. Additionally, cupric chloride is also effective for leaching small amounts of silver in connection to gold ores.

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Appendix

Appendix A: Gold concentration in batch leaching experiment solids samples.

Raw material 1

Experiment	Au (mg/kg)	Ag (mg/kg)
0-sample (1)	1.89	-
0-sample (2)	1.88	1.1
<75 µm	1.98	-
>75 µm	1.61	-
1.1	0.67	-
1.2	0.54	-
1.3	0.53	-
1.4	0.67	-
1.5	0.59	-
1.6	0.75	-
1.7	0.75	-
1.8	0.64	-
1.9	0.41	-
1.10	0.76	-
1.11 (1h)	0.63	1.0
1.11	0.65	0.5
1.12	0.67	0.7
1.13	0.60	0.5
1.14	0.67	0.6
1.15	0.26	0.5
1.16	0.60	0.6
1.17	0.61	0.3
1.18	0.64	0.4
1.19	0.62	0.5

Raw material 2

Experiment	Au (mg/kg)	Ag (mg/kg)
0-sample	4.93	1.6
<45 µm	8.66	2.6
>45 µm	2.92	0.9
2.1	2.37	<0.2
2.2	1.90	<0.2
2.3	2.87	<0.2
2.4	2.84	0.2
2.5	1.80	<0.2
2.6	3.31	<0.2
2.7	2.67	<0.2
2.8	2.38	<0.2
2.9	2.15	<0.2
2.10	3.91	<0.2
2.11	2.30	0.5
2.12	1.92	0.5
2.13	2.70	0.5
2.14	2.44	0.7
2.15	3.19	0.7
2.16	2.44	0.4
2.17	3.27	0.9
2.18	3.34	0.8
2.19	2.54	1.0

Appendix B: Gold concentrations in batch leaching experiment solution samples.

Raw material 1

	t (min)	0	10	30	60	90	120	150	180	210	240	270	300	330	360
E 1.1	c(Au) (mg/l)	<<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1				
E 1.2	c(Au) (mg/l)	<<1	<<1	<<1	<<1	<<1	<<1	<<1	<<1	<<1	<<1				
E 1.3	c(Au) (mg/l)	<<1	0,1	<<1	<<1	<<1	<<1	<<1	<<1	<<1	<<1				
E 1.4	c(Au) (mg/l)	<<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1				
E 1.5	c(Au) (mg/l)	<<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1				
E 1.6	c(Au) (mg/l)	<<1	1.4	1.8	1.6	2.3	1.5	1.6	1.8	1.8	1.8				
E 1.7	c(Au) (mg/l)	<<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1				
E 1.8	c(Au) (mg/l)	<<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1				
E 1.9	c(Au) (mg/l)	<<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1				
E 1.10	c(Au) (mg/l)	<<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1				
E 1.11	c(Au) (mg/l)	0.13	0.13	0.15	0.13	0.15	0.16	0.15							
E 1.12	c(Au) (mg/l)	0.062	0.068	0.076	0.082	0.088	0.094	0.1	0.12	0.12	0.12				
E 1.13	c(Au) (mg/l)	0.059	0.077	0.084	0.086	0.096	0.1	0.1	0.11	0.11	0.12	0.1	0.14	0.15	0.14
E 1.14	c(Au) (mg/l)	0.062	0.072	0.082	0.086	0.091	0.095	0.096	0.087	0.11	0.11				
E 1.15	c(Au) (mg/l)	0.11	0.11	0.13	0.14	0.2	0.15	0.23	0.27	0.29	0.27				
E 1.16	c(Au) (mg/l)	0.057	0.072	0.08	0.082	0.088	0.093	0.093	0.092	0.1	0.1				
E 1.17	c(Au) (mg/l)	0.025	0.017	0.029	0.039	0.043	0.047	0.053	0.053	0.063	0.061				
E 1.18	c(Au) (mg/l)	0.059	0.071	0.081	0.083	0.09	0.09	0.097	0.1	0.082	0.1				
E 1.19	c(Au) (mg/l)	0.068	0.076	0.082	0.092	0.094	0.089	0.1	0.1	0.12	0.081				

Raw Material 2

	t (min)	10	30	60	90	120	150	180	210	240	270	300	330	360
E 2.1	c(Au) (mg/l)	0.15	0.17	0.17	0.22	0.27	0.3	0.31	0.36	0.42				
E 2.2	c(Au) (mg/l)	0.17	0.19	0.19	0.28	0.32	0.35	0.35	0.39	0.41				
E 2.3	c(Au) (mg/l)	0.12	0.14	0.17	0.19	0.21	0.22	0.25	0.29	0.32				
E 2.4	c(Au) (mg/l)	0.11	0.19	0.15	0.12	0.13	0.22	0.24	0.22	0.26				
E 2.5	c(Au) (mg/l)	0.1	0.07	0.11	0.11	0.13	0.14	0.17	0.18	0.2				
E 2.6	c(Au) (mg/l)	0.25	0.27	0.35	0.39	0.46	0.46	0.53	0.54	-				
E 2.7	c(Au) (mg/l)	0.14	0.14	0.18	-	0.22	0.21	0.29	0.26	0.34				
E 2.8	c(Au) (mg/l)	0.1	0.11	0.12	0.12	0.14	0.13	0.15	0.14	0.15				
E 2.9	c(Au) (mg/l)	0.33	0.37	-	0.43	0.42	0.47	0.49	0.51	0.61				
E 2.10	c(Au) (mg/l)	0.04	0.05	0.04	0.05	0.06	0.09	0.07	0.07	0.11				
E 2.12	c(Au) (mg/l)	0.14	0.19	0.24	0.27	0.36	0.36	0.41	0.47	0.5	0.52	0.59	0.59	0.61

Appendix C: Silver concentrations in batch leaching experiment solution samples.

Raw Material 1

	t (min)	10	30	60	90	120	150	180	210	240	270	300	330	360
E 1.11	c(Ag) (mg/l)	0.16	0.15	0.16	0.16	0.17	0.18	0.17						
E 1.12	c(Ag) (mg/l)	0.2	0.21	0.21	0.22	0.23	0.24	0.24	0.28	0.27	0.25			
E 1.13	c(Ag) (mg/l)	0.13	0.18	0.16	0.18	0.17	0.17	0.17	0.17	0.16	0.20	0.17	0.2	0.21
E 1.14	c(Ag) (mg/l)	0.16	0.16	0.16	0.17	0.18	0.18	0.17	0.17	0.19	0.17			
E 1.15	c(Ag) (mg/l)	0.37	0.46	0.39	0.40	0.37	0.3	0.38	0.4	0.39	0.37			
E 1.16	c(Ag) (mg/l)	0.17	0.18	0.17	0.18	0.18	0.19	0.18	0.18	0.19	0.18			
E 1.17	c(Ag) (mg/l)	0.16	0.15	0.15	0.17	0.15	0.16	0.16	0.16	0.17	0.16			
E 1.18	c(Ag) (mg/l)	0.14	0.12	0.14	0.15	0.13	0.15	0.14	0.14	0.12	0.13			
E 1.19	c(Ag) (mg/l)	0.18	0.5	0.19	0.16	0.17	0.16	0.16	0.15	0.17	0.12			

Raw Material 2

	t (min)	10	30	60	90	120	150	180	210	240	270	300	330	360
E 2.1	c(Ag) (mg/l)	0.52	0.55	0.56	0.61	0.55	0.58	0.59	0.66	0.62				
E 2.2	c(Ag) (mg/l)	0.55	0.53	0.62	0.58	0.57	0.58	0.58	0.56	0.57				
E 2.3	c(Ag) (mg/l)	0.69	0.69	0.72	0.7	1,46	0.85	0.74	0.71	0.71				
E 2.4	c(Ag) (mg/l)	0.4	0.61	0.42	0.41	0.39	0.39	0.42	0.49	0.41				
E 2.5	c(Ag) (mg/l)	0.5	1,74	0.37	0.38	0.39	0.38	0.39	0.37	0.38				
E 2.6	c(Ag) (mg/l)	0.69	0.7	0.68	1.29	0.69	0.78	0.75	0.79	-				
E 2.7	c(Ag) (mg/l)	0.55	0.57	0.82	-	0.55	3,09	0.6	4,45					
E 2.8	c(Ag) (mg/l)	0.5	0.49	0.51	0.5	0.5	0.5	0.52	0.5	0.51				
E 2.9	c(Ag) (mg/l)	0.55	0.54	-	0.55	0.59		0.6	0.57	0.59				
E 2.10	c(Ag) (mg/l)	0.56	0.57	0.58	0.6	0.65	0.62	0.64	0.65	0.68				
E 2.12	c(Ag) (mg/l)	0.63	0.64	0.67	0.69	0.72	0.73	0.76	0.83	0.84	0.87	0.89	0.9	0.92

Appendix D: Added HCl as function of time.

Raw material 1

	t (min)	0	10	30	60	90	120	150	180	210	240	270	300	330	Total
E 1.1	ml	22	17	14	8	12	9	5	4	3					94
E 1.2	ml	19	14	8	7	2	3	2	3	2					60
E 1.3	ml	12	9	9	8	5	4	3	2	3					55
E 1.4	ml	21	15	13	10	14	8	9	7	7					104
E 1.5	ml	20	18	11	7	10	6	8	4	4					88
E 1.6	ml	23	15	15	12	9	6	8	4	3					95
E 1.7	ml	15	14	10	8	5	5	3	3	2					65
E 1.8	ml	20	16	13	10	7	5	5	4	3					83
E 1.9	ml	20	16	8	8	9	8	4	3	3					79
E 1.10	ml	17	12	11	6	4	4	3	3	3					63
E 1.11	ml	18	15	12	9	11									65
E 1.12	ml	22	18	16	14	11	9	5	6	4					105
E 1.13	ml	21	15	11	9	7	5	4	3	2	1	1	0	1	80
E 1.14	ml	23	15	15	11	12	11	9	7	8					111
E 1.15	ml	18	14	13	15	7	5	4	2	2					80
E 1.16	ml	19	15	11	11	9	6	6	2	1					80
E 1.17	ml	21	13	12	15	7	3	5	1	3					80
E 1.18	ml	20	16	14	12	10	8	7	11	2					100
E 1.19	ml	17	13	11	10	7	4	3	4	1					70

Raw material 2

	t (min)	0	10	30	60	90	120	150	180	210	240	270	300	330	Total
E 2.1	ml	3	2	1	1	1	1	1	1	1					12
E 2.2	ml	3	2	1	1	1	1	1	1	1					12
E 2.3	ml	2	1	1	1	1	1	1	0	0					8
E 2.4	ml	3	2	1	1	1	1	1	1	0					11
E 2.5	ml	3	1	1	1	1	1	0	0	0					8
E 2.6	ml	3	3	2	2	1	1	1	1	1					15
E 2.7	ml	3	3	1	1	2	1	1	1	1					14
E 2.8	ml	3	2	2	1	1	1	1	1	0					12
E 2.9	ml	2	1	0	2	0	0	0	0	0					5
E 2.10	ml	4	2	1	2	1	1	1	1	0					13
E 2.11	ml	2	1	0	0	1	0	0	0	0					4
E 2.12	ml	2	1	2	0	0	0	0	0	0	0	1	0	0	6
E 2.13	ml	2	2	0	0	0	1	0	0	0					5
E 2.14	ml	3	1	0	1	0	0	0	1	0					6
E 2.15	ml	3	1	1	1	1	0	1	0	0					8
E 2.16	ml	2	1	0	0	0	0	0	1	0					4
E 2.17	ml	1	0	0	0	0	0	0	0	0					1
E 2.18	ml	2	0	0	0	0	0	0	0	0					2
E 2.19	ml	2	0	0	1	0	0	0	0	0					3

Appendix E: Redox potential during sampling.

Raw material 1

	t (min)	0	10	30	60	90	120	150	180	210	240	270	300	330	360
E 1.1	(mV vs. Ag/AgCl	682	486	482	499	510	520	536	554	571	589				
E 1.2	(mV vs. Ag/AgCl	653	494	554	583	595	602	609	615	612	620				
E 1.3	(mV vs. Ag/AgCl	693	497	509	534	568	596	610	619	625	623				
E 1.4	(mV vs. Ag/AgCl	622	446	439	448	442	515	542	561	578	582				
E 1.5	(mV vs. Ag/AgCl	700	476	480	496	515	535	557	579	598	608				
E 1.6	(mV vs. Ag/AgCl	702	428	435	446	463	486	517	548	579	595				
E 1.7	(mV vs. Ag/AgCl	685	472	480	516	545	583	602	615	622	625				
E 1.8	(mV vs. Ag/AgCl	674	458	468	490	519	548	570	577	590	589				
E 1.9	(mV vs. Ag/AgCl	716	484	493	504	518	538	568	601	614	621				
E 1.10	(mV vs. Ag/AgCl	653	462	514	551	563	570	577	580	586	588				
E 1.11	(mV vs. Ag/AgCl	691	479	481	488	494	499								
E 1.12	(mV vs. Ag/AgCl	636	479	486	501	512	533	552	568	583	597				
E 1.13	(mV vs. Ag/AgCl	691	471	487	492	497	503	508	513	518	532	535	541	550	547
E 1.14	(mV vs. Ag/AgCl	664	449	459	478	494	514	531	547	563	576				
E 1.15	(mV vs. Ag/AgCl	709	523	533	565	621	639	647	651	655	659				
E 1.16	(mV vs. Ag/AgCl	680	472	472	476	489	492	502	509	518	527				
E 1.17	(mV vs. Ag/AgCl	648	451	450	455	470	471	475	497	503	524				
E 1.18	(mV vs. Ag/AgCl	696	479	487	488	492	493	497	503	506	510				
E 1.19	(mV vs. Ag/AgCl	675	455	457	468	482	495	506	516	528	538				

Raw material 2

	t (min)	0	10	30	60	90	120	150	180	210	240	270	300	330	360
E 2.1	(mV vs. Ag/AgCl	681	527	540	561	574	582	588	591	591	593				
E 2.2	(mV vs. Ag/AgCl	672	544	571	576	580	583	589	590	589	591				
E 2.3	(mV vs. Ag/AgCl	663	544	554	573	589	588	592	592	597	599				
E 2.4	(mV vs. Ag/AgCl	656	498	514	537	549	552	555	556	559	562				
E 2.5	(mV vs. Ag/AgCl	674	561	566	578	598	604	606	608	611	612				
E 2.6	(mV vs. Ag/AgCl	686	531	545	568	580	591	593	595	597	599				
E 2.7	(mV vs. Ag/AgCl	682	531	535	553	574	588	592	596	594	594				
E 2.8	(mV vs. Ag/AgCl	658	537	553	563	574	570	566	575	578	574				
E 2.9	(mV vs. Ag/AgCl	698	564	563	573	586	593	596	598	600	601				
E 2.10	(mV vs. Ag/AgCl	681	527	540	561	574	582	588	591	591	593				
E 2.11	(mV vs. Ag/AgCl	686	549	555	559	576	582	587	589	591	592				
E 2.12	(mV vs. Ag/AgCl	674	541	544	557	571	582	586	588	594	597	600	601	604	606
E 2.13	(mV vs. Ag/AgCl	642	524	527	540	547	555	569	565	572	579				
E 2.14	(mV vs. Ag/AgCl	683	544	535	533	537	532	538	553	567	575				
E 2.15	(mV vs. Ag/AgCl	655	517	526	547	561	565	568	571	576	579				
E 2.16	(mV vs. Ag/AgCl	679	549	548	556	564	575	579	584	586	589				
E 2.17	(mV vs. Ag/AgCl	630	533	534	531	533	539	544	537	542	539				
E 2.18	(mV vs. Ag/AgCl	677	538	553	555	572	565	573	564	577	576				
E 2.19	(mV vs. Ag/AgCl	693	556	563	576	585	587	587	582	592	584				

Appendix F: Mass of filtered and dry residues.

Raw material 1		Raw material 2	
Experiment	m (g)	Experiment	m (g)
1.1	402.03	2.1	384.31
1.2	394.25	2.2	341.27
1.3	407.31	2.3	388.36
1.4	390.75	2.4	380.15
1.5	426.03	2.5	472.4
1.6	373.4	2.6	283.26
1.7	409.75	2.7	384.62
1.8	411.54	2.8	379.87
1.9	409.33	2.9	361.05
1.10	420.65	2.10	421.14
1.11	407.32	2.11	377.75
1.12	418.59	2.12	370.9
1.13	396.42	2.13	368.6
1.14	397.11	2.14	359.79
1.15	429.43	2.15	419.35
1.16	396.75	2.16	404.54
1.17	421.39	2.17	371.11
1.18	408.66	2.18	369.67
1.19	398.86	2.19	359.59

Appendix G: Final solution volume.

Raw material 1		Raw material 2	
Experiment	V (ml)	Experiment	V (ml)
1.1	1950	2.1	1770
1.2	1990	2.2	1900
1.3	1940	2.3	1770
1.4	2010	2.4	1940
1.5	1930	2.5	1890
1.6	1990	2.6	1870
1.7	1870	2.7	1970
1.8	2060	2.8	1990
1.9	2080	2.9	1780
1.10	1850	2.10	1650
1.11	2010	2.11	1650
1.12	1720	2.12	1290
1.13	1570	2.13	1650
1.14	1850	2.14	1730
1.15	1890	2.15	1600
1.16	1960	2.16	1830
1.17	2200	2.17	2050
1.18	1780	2.18	2100
1.19	1790	2.19	2000